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Schiff-based Pd(II)/Fe(III) bimetallic self-assembly monolayer—preparation, structure, catalytic dynamic and synergistic



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ABSTRACT

Graphene oxide supported Pd (II)/Fe (III) bimetallic catalytic monolayer (denoted as GO@H-Pd/Fe) was prepared and characterized. Its catalytic performances for Suzuki coupling reaction, synergetic effect and catalytic mechanism were systematic investigated. Results showed that orientation, composition and distribution of catalyst had efficient effect on catalytic activity. Catalytic activity of $GO@H-Pd_{0.10}/Fe_{0.90}$ was 475 times more than that of GO@H-Pd due to the ordered catalytic monolayer immobilized on GO, proper ratio of Pd/Fe and the synergetic effect between Pd(II) and Fe(III) which could form active cluster containing Pd and Fe. The Pd(II) could be made more negative by transferring electron from GO to Fe(III) via ligand and then to Pd, improving its catalytic activity since it was easy for oxide addition. It also exhibited better stability and recyclability at least 8 times due to proper functional ligand and support. Deactivation mechanism was confirmed to be the aggregation of active centre during the recycling. Heterogeneous catalytic mechanism was also proved by poison test, hot filtration and ReactIR. The results of ReactIR presented different dynamic catalytic process for $GO@H-Pd_{0.10}Fe_{0.90}$ and homogeneous catalyst (Li₂PdCl₄/FeCl₃·6H₂O). The activation energies were 9.7 KJ/mol and 3.7 KJ/mol obtained for heterogeneous also investigated by ReactIR, with which that $GO@H-Pd_{0.10}Fe_{0.90}$ catalytic activity was higher than that of homogeneous catalyst could be confirmed.

1. Introduction

Precious metal catalysis show important ways in the bond formation in organic synthesis, modern medicine and materials science, in which palladium-catalyzed Suzuki-Miyaura, Heck, and Negishi couplings are indispensable [1,2]. Palladium as a precious metal is uneconomical in using and has limited reserves [3]. To solve this problem, other nonprecious metals such as iron [4,5], copper [6,7], cobalt [8–10] and nickel [11,12] have been systematic studied [13,14].

Among of them, iron is a non-precious and tremendous amount, which has various valences and critical function in bio-systems. It is also an ideal green catalyst and become one of the most active research fields in recent years [15–19]. The reactions catalyzed by iron are also spring up, including oxidation, reduction, coupling, substitution, addition, ring addition and ring expansion, multi-component reaction and so on. The coupling reactions catalyzed by iron catalyst have achieved many results, but meet many problems, such as strict reaction condition, the large dosage of catalyst, the rule of the transform of valence

states in catalysis. Therefore, designing and preparing novel iron catalysts with high catalytic activity will be great significance.

As we know, although homogeneous catalysts with high efficiency and practical applications, they are significantly restricted to the separation of soluble catalysts from the reaction systems and recycling [20]. Application of heterogeneous catalysts has received tremendous scientific and industrial attention because of their high activity and recyclability [21–26]. Among heterogeneous catalysts, hetero-bimetallic catalysts which doped with non-precious metals have attracted extensive attentions due to greatly reduced the amount of palladium, and the cost to some extent. Especially, the second metal could induce the special properties [27–32].

Among various supporting materials used in heterogeneous catalysis, carbon nanomaterials, such as grapheme oxide (**GO**) has attracted enormous attention due to its unique chemical, physical properties [33] used in some application [34,35]. Especially, graphene oxide rich with hydroxyls, carboxyls and epoxides on the planar surfaces which is readily available functionalized [36,37], such as suitable textural

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Scheme 1. Preparation of GO@H-Pd/Fe monolayer.

design [38], doping (N-doping, P-doping, S-doping and B-doping) [39] and noble metal loading [40].

According to the complexing ability, numerous studies showed that carbon nano-structure modified by ligands having amino and imine groups had more surface binding sites of the meal, stability and utility compare to nitrogen-free. In previous studies, we have reported that functional groups on surface of support materials had significant impact to the activity of catalyst [41]. On the one hand, it allowed for anchoring and better dispersion for the catalytic nano-particles on the support surface [42] due to the electron effect of nitrogen and the modified process improved the stability of the produced catalysts because of enhanced of π binding. Therefore, combining the advantages of proper supports, ligands, different metals, self-assembly way [43-45] and measuring methods will made it easy for constructing new catalyst with special properties and deeply investigating the mechanism for improving the catalytic activity. The control of chemical processes through online technology attracted much more attention, such as IR, NIR, Raman, ReactIR [46,47]. They have the advantages over offline analysis for avoiding hazardous substances. Suzuki-Miyaura reaction process also could be detected by ReactIR, with which the reaction activation energy of homogeneous and heterogeneous catalysts was calculated based on ReactIR data.

In this paper, a ligand having Schiff-base group was chemically grafted to the surface of graphene oxide, and the ligation site of metal ions was formed by further modification. The palladium and iron were immobilized by coordination bond toward synthesis of a reusable and recoverable Pd/Fe bimetallic heterogeneous catalytic monolayer. Mechanism of Pd/Fe catalyst during catalyzing reaction, deactivation during the recycle and synergetic effect were detailed investigated.

2. Experimental

Table 1

2.1. Regents and equipments

Regents were obtained from commercial. Characterization equipments were presented in supporting information section.

2.2. Preparation of the amino modified graphene oxide and GO@H-Pd/Fe

It was presented in Supporting information section [48].

2.3. Suzuki coupling reaction catalyzed by GO@H-Pd/Fe

It was performed in Supporting information section [49].

3. Results and discussion

3.1. Preparation and characterization of GO@H-Pd/Fe

GO@H-Pd/Fe catalytic monolayer was prepared as depicted in Scheme 1

XRD of GO@H-Pd/Fe in fabrication process were measured (Figure S1). The diffraction peaks at 11.27° and 42.40° designed to the planes of GO [50,51]slightly shift towards a higher angle compared with that of GO after modified with nitrogen group, followed by loading of Pd and Fe due to molecular intercalation and also sonication. Characteristic diffraction peaks at 21.09° was the plane of **rGO**. The reason is that the modifying with nitrogen group and load of Pd and Fe covered oxygen on the surface of GO. Furthermore, the ordered catalytic monolayer was confirmed by the XRD analysis of Si@H-Pd/Fe at different grafting processes (Figure S2). The characteristic sharp small angle diffraction peaks at about 1.4°, and the peak strength and peak width were slightly changed with the self-assembling. It could be seen that the monolayer of ordered self-assembled catalyst were grafted on silicon. The catalytic monolayer also could also be certificated by the water contact angle's (WCA) analysis, in which the different properties of monolayer surface at different grafting processes were observed. (Figure S3)

FTIR of preparation process for **GO@H-Pd/Fe** were measured as shown in Figure S4. Peaks at 3430 cm^{-1} , 1729 cm^{-1} , 1622 cm^{-1} , 1221 cm^{-1} and 1053 cm^{-1} were corresponded to stretching of O–H and C=O, vibration of C–O, stretching of C–OH and epoxy on **GO**. After ligand modification, characteristic peaks at 1105, 1042 cm^{-1} for Si–O and 1636 cm⁻¹ for free C=N in **H-GO** could be observed. In the case of **GO@H-Pd/Fe**, the peak of C=N red shifted which depended on coordination with the Fe and Pd ions [52].

Raman spectra of GO, H-GO, and GO@H-Pd/Fe exhibited the disorder. The characteristic peak of GO at about 1336 and 1586 cm⁻¹ were D band and G band, respectively in Figure S5 [53]. The ratio of I_D/I_G showed a general trend of decrease from 1.05 to 1.01 and 0.99 which reflected the number of Csp² atoms increased during fabricating processes of GO@H-Pd/Fe [54,55]. There were two possible reasons, one reason was the change of C sp² atoms caused by anchoring ligand, resulting in the low ratio of oxygen. Another reason was that ligand graft and metal coordination. The G band at 1584 cm⁻¹ shifted to 1576 cm⁻¹ as ligand was anchored and then to 1585 cm⁻¹ when GO@ H-Pd/Fe was formed. The peak shifting could be explained by that the gradually change of local stress was changed by the modifying [56,57].

The elements of **GO@H-Pd/Fe** monolayer was measured with XPS as shown in Figure S6. Peaks for N 1s, Cl 2p, C 1s, Si 2s, O 1s, Pd 3d and Fe 2p could be clearly observed (Figure S6a). Two bands at 338.0 and 343.2 eV were the character binding energy of Pd (II) (Figure S6b). Fe 2p presented two bands at 711.9 and 725.0 eV ascribed to the binding energy of iron (III) (Figure S6c).

SEM pictures of graphene oxide (GO), H-GO, GO@H-Pd/Fe were measured (Figure S7). Layer-like structure could be observed (Figure

influences of the ratio of Pd/Fe on catalytic performance.								
Catalyst	Pd $(mol \cdot g^{-1})$	Fe $(mol \cdot g^{-1})$	Time (h)	Isolated yield (%)	TON(mol mol _{Pd} ⁻¹)	TOF (h ⁻¹)		
GO@H-Pd	2.49×10^{-4}	-	12	99	199	17		
GO@H-Fe	_	2.42×10^{-4}	12	trace	-	-		
GO@H-Pd _{0.01} Fe _{0.99}	$1.93 imes 10^{-6}$	$2.19 imes 10^{-4}$	12	71	18394	1533		
GO@H-Pd _{0.05} Fe _{0.95}	$4.28 imes 10^{-5}$	2.14×10^{-4}	12	87	1016	85		
GO@H-Pd _{0.10} Fe _{0.90}	$5.33 imes 10^{-5}$	$1.93 imes 10^{-4}$	12	95	892	74		

^a Reaction condition: PhB(OH)₂ (0.25 mmol), 4-bromotoluene (0.25 mmol), K₂CO₃ (0.5 mmol), catalyst 5 mg, solvent (50% aqueous alcohol 4 mL) at 70 °C.

Table 2

Optimization of Suzuki-Miyaura reaction conditions using GO@H-Pd_{0.10}Fe_{0.90}.

Entry	Base	Solvent	Time (h)	T (°C)	Isolated yield (%)	$TOF(h^{-1})^{f}$
1	K ₂ CO ₃	H ₂ O	12	70	70	31
2	K_2CO_3	EtOH	12	70	8	6.3
3	K_2CO_3	DMF	12	70	6	4.7
4	K_2CO_3	MeOH	12	70	trace	-
5	K_2CO_3	H ₂ O:EtOH(2:1)	12	70	99	77
6	K_2CO_3	H ₂ O:EtOH(3:1)	12	70	99	77
7	K_2CO_3	Toluene	12	70	trace	-
8	Na_2CO_3	H ₂ O:EtOH(3:1)	12	70	99	77
9	K ₃ PO ₄	H ₂ O:EtOH(3:1)	12	70	99	77
10	NaOH	H ₂ O:EtOH(3:1)	12	70	93	73
11	NaOAc	H ₂ O:EtOH(3:1)	12	70	39	31
12	NaHCO ₃	H ₂ O:EtOH(3:1)	12	70	92	72
13	Et ₃ N	H ₂ O:EtOH(3:1)	12	70	95	74
14	Na ₂ CO ₃	H ₂ O:EtOH(3:1)	12	70	99^{b}	129
15	Na_2CO_3	H ₂ O:EtOH(3:1)	12	70	98 ^c	383
16	Na_2CO_3	H ₂ O:EtOH(3:1)	1	70	92^b	4318
17	Na ₂ CO ₃	H ₂ O:EtOH(3:1)	2	70	99^b	2324
18	Na ₂ CO ₃	H ₂ O:EtOH(3:1)	12	60	94 ^b	368
19	Na ₂ CO ₃	H ₂ O:EtOH(3:1)	12	50	88^b	344
20	Na_2CO_3	H ₂ O:EtOH(3:1)	12	30	35 ^b	137
21	Na_2CO_3	H ₂ O:EtOH(3:1)	2	70	94^d	4412
22	Na ₂ CO ₃	H ₂ O:EtOH(3:1)	2	70	86 ^e	8074

^{*a*} Reaction condition: PhB(OH)₂ (0.25 mmol), 4-bromotoluene (0.25 mmol), Base (0.5 mmol), **GO@H-Pd_{0.10}Fe_{0.90}** 5 mg, solvent (4 mL) at 70 °C. ^{*b*} **GO@H-Pd_{0.10}Fe_{0.90}** 3 mg, ^{*c*} **GO@H-Pd_{0.10}Fe_{0.90} 1 mg. ^{***d***} PhB(OH)₂ (0.55 mmol), 4-bromotoluene (0.5 mmol), Base (1 mmol), GO@H-Pd_{0.10}Fe_{0.90}** 1 mg, ^{*e*} PhB(OH)₂ (1 mmol), 4-bromotoluene (1 mmol), Base (2 mmol), **GO@H-Pd_{0.10}Fe_{0.90}** 1 mg. ^{*f*} 1 mg **GO@H-Pd_{0.10}Fe_{0.90} containing** 0.0000533 mmol Pd.

Table 3 Influences of support and the functioned structure on catalytic performance.

Entry	Catalyst	Pd loading(mmol·mg ^{-1})	Yield (%)
1	GO	-	0^b
2	H-GO	-	0^c
3	Li ₂ PdCl ₄ /FeCl ₃ ·6H ₂ O	0.0000533	76^d
4	$H + Li_2PdCl_4/FeCl_3 \cdot 6H_2O$	0.0000533	35
5	GO + Li ₂ PdCl ₄ /FeCl ₃ ·6H ₂ O	0.0000533	53
6	H-GO + $Li_2PdCl_4/FeCl_3 \cdot 6H_2O$	0.0000533	50
7	GO-Pd _{0.10} Fe _{0.90}	0.0000254	15^e
8	GO@H-Pd _{0.10} Fe _{0.90}	0.0000533	99 ^f
9	Silica@H-Pd _{0.10} Fe _{0.90}	0.000741	70 ^g

^{*a*} Reaction condition: PhB(OH)₂ (0.25 mmol), 4-bromotoluene (0.25 mmol), Na₂CO₃ (0.5 mmol), catalyst 5 mg, solvent (25% aqueous alcohol 4 mL) at 70 °C for 2 h. ^{*b*} GO 1 mg. ^{*c*} H-GO 1 mg. ^{*d*} Li₂PdCl₄ 0.000053 mmol and FeCl₃·6H₂O. ^{*e*} GO-Pd_{0.10}Fe_{0.90} 1 mg. ^{*f*} GO@H-Pd_{0.10}Fe_{0.90} 1 mg. ^{*g*} Silica@H-Pd_{0.10} Fe_{0.90} 1 mg.

S7a). After being grafted with nitrogen group, more crumpling appeared because of the chemical modifications (Figure S7b). Neat sheet like structure were also obtained after complexed with Pd and Fe,

which demonstrated that imine palladium and iron complexes were orderly modified to graphene oxide sheet (Figure S7c).

SEM-EDS of **GO@H-Pd/Fe** were measured (Figure S8), in which palladium and iron were presented on the surface of the catalyst. It was clear that relative amount of palladium and iron with different electron layers from the distribution diagram.

TEM images of **GO**, **H-GO**, **GO@H-Pd/Fe** were also obtained (Figure S9), in which the clear sheet like structure was obtained (Figure S9a). After modification with nitrogen group and metals, similar sheet like structures could be seen (Figure S9b and Figure S9c), suggesting that the morphology of **GO** maintained during the modification. The results obtained above exhibited that ordered **GO@H-Pd/Fe** catalytic monolayer on **GO** was fabricated.

To further characterize the S_{BET} (Specific surface area) of corresponding pore size distribution about ${\bf GO}@{\bf H-Pd}/{\bf Fe},\ N_2$ adsorption-desorption isotherms were actualized. As depicted in Figure S10a, it could be clearly observed that the ${\bf GO}$ and ${\bf H-GO}$ isotherms were ascribed as type IV with a H4 hysteresis loop $(12.0295\,m^2\,g^{-1},\ 4.2302\,m^2\,g^{-1},\ respectively).The <math display="inline">{\bf GO}@{\bf H-Pd}/{\bf Fe}$ isotherm as shown in Figure S10b was ascribed as type IV with a H3 hysteresis loop $(4.2507\,m^2\,g^{-1})$ [58,59], proving the existence of mesoporous

Table 4

Comparison of the results for Suzuki reaction catalyst by GO@H-Pd_0.10Fe0.90 catalyst with that by Pd and Fe catalysts reported.

Entry	Catalyst	Reaction conditions	Х	Yield (%)	TOF_{pd} (h ⁻¹)	Ref
This work	GO@H-Pd _{0.10} Fe _{0.90} (0.0106 mol%Pd)	Na ₂ CO ₃ , EtOH:H ₂ O, 2 h, 70°C	Br	86	8074	-
2	Pd complex 3(0.06 mol% Pd)	K ₂ CO ₃ , <i>i</i> PrOH:H ₂ O, 30 h, RT	Br	94	26	59
3	Pd-Fe ₃ O ₄ /NCs (1 mol%Pd)	Na ₂ CO ₃ , DEM:H ₂ O, 24 h, 100°C	Br	70	3	60
4	BIO-IM-Pd (0.5 mol%)	K ₂ CO ₃ , solvent-free, 1 h, 120°C	Br	84	84	61
5	PdCl ₂ /P-Fe-C(ax) (1.5 mol% Pd)	K ₂ CO ₃ , DMF 8 h, 90°C	Cl	42	350	62
6	Pd/Fe ₃ O ₄ /s-G (0.15 mol% Pd)	K_2CO_3 , EtOH:H ₂ O, 30 min, 80°C	Br	97	1293	63
7	HMMS-salpr-Pd (1 mol%)	K ₂ CO ₃ , EtOH:H ₂ O, 7 h, 70°C	Br	76	11.5	64

S	uzuki-Miyaura	reaction	of aryl	halides	with	different	aryl-boronic	acids.
_								

Entry	Ar–X	Ar'-B(OH) ₂	Product	Yield(%)
1	I	B(OH)2		99
2	MeO	B(OH)2	MeO-	99
3	Br	—В(ОН) ₂	$\bigcirc - \bigcirc$	99
4	$O_2N - Br$	B(OH)2	0 ₂ N-	99
5	NC	B(OH)2	NC	99
6	F ₃ C-	B(OH) ₂	F ₃ C-	96
7	H ₂ N-Br	B(OH) ₂	H ₂ N-	99
8	MeO-	B(OH) ₂	мео-	99
9	Br	B(OH)2	MeO	99
10	MeO Br	B(OH)2	OMe	94
11	ОМе	B(OH)	онс-	99
12	Br	B(OH) ₂		92
13	OHC Br	B(OH)2	СНО	80
14		B(OH)2		11
15		B(OH)2	0 ₂ N-	21
16	MeO-Cl	B(OH) ₂	MeO	15
17	Br	MeO-	OMe	99
18	Br	MeO B(OH)2		95
19	Br			80
20	——————————————————————————————————————	B(OH) ₂		85
21	————Br	NB(OH) ₂		trace
22	Br	N_{N} B(OH) ₂		10
23	——————————————————————————————————————	B(OH) ₂		5

(continued on next page)



^a Reaction condition: Ar'-B(OH)₂ (0.25 mmol), Ar-X (0.25 mmol), Base (0.5 mmol), GO@H-Pd_{0.10}Fe_{0.90} 1 mg, solvent (25% aqueous alcohol 4 mL) at 70 °C for 2 h.



Fig. 1. The recycle experiments of GO@H-Pd_{0.10}Fe_{0.90}.

materials (from 2 to 50 nm) [60]. It was the evident that S_{BET} of **GO@H-Pd/Fe** was smaller than that of **GO** due to modification with catalyst.

EIS (electrochemical impedance spectroscopy) spectra are widely used to understand the transfer efficiency of electrons. Figure S11 showed exhibits the EIS Nynquist plots of GO, H-GO and GO@H-Pd/Fe sample. In principle, the arc in EIS spectra implies the electrochemical reaction impedance of catalysts loaded on the Ni foam electrodes. The smaller arc implies the faster transfer efficiency of electrons and lower transfer resistance with low recombination probability of electrons. Notably, the catalyst GO@H-Pd/Fe has the smallest diameter than GO and H-GO, suggesting that GO@H-Pd/Fe shows superior charge transfer ability.

3.2. Catalytic properties for Suzuki coupling reactions

3.2.1. Influences of the ratio of Pd/Fe on catalytic performance

As shown in Table 1, only trace amounts of products were produced with **GO@H-Fe** under the reaction condition (at 70 °C, 12 h, 2 mmol K₂CO₃ in aqueous ethanol (1:1). However, using **GO@H-Pd**_{0.10}**Fe**_{0.90} as a catalyst 95% isolated yield could be obtained. Considering the cost and green requirement, **GO@H-Pd**_{0.10}**Fe**_{0.90} was chosen for next catalytic research.

3.2.2. Catalytic properties of GO@H-Pd_{0.10}Fe_{0.90}

The catalytic performance of **GO@H-Pd_{0.10}Fe_{0.90}** for Suzuki coupling reaction was carried out with different solvents and bases (Table 2, entries 1–13). 99% yield of 4-phenyltoluene was obtained under optimization condition (70 °C, 12 h, 2 mmol Na₂CO₃, aqueous ethanol (3:1) (entry 8). Furthermore, even though the dosage of catalyst and reaction time were reduced (1 mg, 2 h), 99% yield could be obtained (entry 17). When temperature was decreased, the yield slightly decreased (Table 2, entries 18–20). There was still a high isolated yield of expanded substrate (Table 2, entries 21, 22).

Comparison tests were designed for understanding the effects of support and ligand on the catalytic properties (Table 3). No targets were obtained by **GO** or **H-GO** (entries 1, 2). The inference of **GO** added into catalytic system was studied (entries 3–6). 76% yield was obtained by Li₂PdCl₄/ FeCl₃·6H₂O (entry 3), 35% yield by Ligand/Li₂PdCl₄/ FeCl₃·6H₂O (entry 4), 53% yield by **GO**/Li₂PdCl₄/FeCl₃·6H₂O, 50% yield by **GO**/Ligand/Li₂PdCl₄/FeCl₃·6H₂O, 50% yield by **GO**/Ligand/Li₂PdCl₄/FeCl₃·6H₂O, 15% yield by **GO**·Pd_{0.10}**Fe**_{0.90}, indicating that ligands and its orientation played a crucial role for forming regular catalytic monolayer. On the other word, the coordination between self-assembly ligands and metallic atoms was efficient. **GO@H-Pd**_{0.10}**Fe**_{0.90} monolayer linked with **GO** by self-assembly way presented higher catalytic properties (entry 8). The reason was that the catalytic active site could be isolated on the surface of



Fig. 2. SEM images of the process of catalyst and reused catalyst (a) at 0 min, (b) at 60 min, (c) at 120 min, (d) after 4th run, (e) after 8th run.



Fig. 3. TEM images of the process of catalyst and reused catalyst (a) at 0 min, (b) at 60 min, (c) at 120 min, (d) after 4th run, (e) after 8th run.



Fig. 4. HRTEM of **GO@H-Pd**_{0.10}**Fe**_{0.90} catalysts at different catalytic time: (a) at 60 min; (b) at 120 min; (c) after 4th run; (d) after 8th run. Histogram of the Pd^0 nano-cluster diameters at 60 min: 3.36 nm in (a), from a sample population of 140; 120 min: 3.49. nm in (b), from 70; after 4th run 3.77 nm in (c), from 29; after 8th run 3.87 nm in (d), from 29 particles.



Fig. 5. XPS of the process of catalyst and reused catalyst (a) Pd 3d, (b) Fe 2p, (c) Pd 3d, B 1 s, Br 3p.



Scheme 2. Proposed formation of Pd/Fe active centre.

monolayer and prevented from aggregating by the ligand [61,62]. Compared with Silica@H-Pd/Fe, isolated yield of GO@H-Pd_{0.10}Fe_{0.90} was not only high yield, but also high TOF value. It was attributed to GO@H-Pd_{0.10}Fe_{0.90} could easily disperse in solution (Table 3). These results could be interpreted that not only good dispersivity of GO@H-Pd_{0.10}Fe_{0.90}, but also the efficiently electronic transferring between Pd/Fe complex and GO. What is more, GO could promotes mass transfer and made the substrates contact with the supported catalytic active centre easily [63]. At mean time, the function of GO in GO@H-Pd_{0.10}Fe_{0.90} for improving catalytic performance was its electron rich, not its bigger S_{BET} according to the data of GO@H-Pd_{0.10}Fe_{0.90}.

The catalytic activities of $GO@H-Pd_{0.10}Fe_{0.90}$ compared with other Pd and Fe complex reported were listed in Table 4. Impressively, a low amount of $GO@H-Pd_{0.10}Fe_{0.90}$ (0.0106 mol%) with higher TOF was presented compared with other catalyst, indicating that ordered $GO@H-Pd_{0.10}Fe_{0.90}$ self-assembly monolayer presented some advantage over other catalysts reported.

Suzuki coupling reaction catalyzed by **GO@H-Pd**_{0.10}/**Fe**_{0.90} was carried out for screening the scope of substrates. Quantitative yield of 4-phenyltoluene (> 99%) with aryl iodide was obtained (Table 5, entry 1, 2). Higher yields were obtained for aryl bromides having electron-releasing or electron-withdrawing groups (Table 5, entry 3–13). Mean-while, different substituting position of aryl bromides, the yield of

ortho-substituted aryl bromides was lower than that of *para*-substituted or meta-substituted due to steric effect (Table 5, entries 8–13). However, the results for chlorobenzene derivatives were not satisfactory (Table 5, entries 14–16). Further, coupling phenylboronic derivatives and heterocyclic borate with 4-bromotoluene (Table 5, entries 17–24), comparing to phenylboronic derivatives, heterocyclic borate with 4-bromotoluene showed lower reactivity. This might be that the catalyst has poor applicability to heterocyclic substrate. On the other hand, in Table 5, compare Entry 1 with 3, aryl iodides react faster than bromides or chlorides, in order to investigate the catalytic activity deeply we optimize the reaction for iodo (Table S1). ¹H and ¹³CNMR spectra of biaryl products have provided in supporting information (Figure S12, Figure S13, Figure S14, Figure S15, Figure S16 and Figure S17).

For recycle experiments, the performance of **GO@H-Pd_{0.10}Fe_{0.90}** reusability was investigated, in which it showed better stability upon reuse (Fig. 1). Although the isolated yield dropped slightly at the sixth time, the cycle could reach nine times by extending reaction time (Fig. 1). The reason was the loss of the catalytic active centre during recycling was studied according to ICP-AES and the remaining amount was Pd: 8.79×10^{-6} mmol/mg, Fe: 6.35×10^{-5} mmol/mg at sixth recycle.

3.3. Deactivation mechanism of the GO@H-Pd_{0.10}Fe_{0.90} catalysts

Deactivation of catalysts means a loss of catalytic activity when recycled in several times [64]. To illuminate the deactivation mechanism was of great significance for improving the catalytic activity and stability.

The SEM images of the catalyst recycled at 8th run exhibited almost no changes in the morphology shown in Fig. 2. TEM images of **GO@H-Pd**_{0.10}**Fe**_{0.90} catalysts were also obtained after 1 h, 2 h, the 4th and the 8th run (Fig. 3), in which it could be seen that slight agglomeration appeared at 4th and 8th run. The morphology and arrangements of **GO@H-Pd**_{0.10}**Fe**_{0.90} were the similar lattice fringes (Fig. 4a-d) at different catalytic time. The presence of polydisperse, regular-shaped Pd (1 1 1) nano-clusters was 0.225 nm. The particle size of metal changed a little into large size, which implied that deactivation had relation to the aggregation of active centre and the loss of catalyst during recycling.



Fig. 6. ReactIR plots with time for the resultant of Suzuki reaction at 70 °C (a) 3D map catalyzed by $GO@H-Pd_{0.10}Fe_{0.90}$, (b) 3D map catalyzed by $Li_2PdCl_4 + FeCl_3GH_2O$, (c) Kinetic analysis of catalytic reaction of $GO@H-Pd_{0.10}Fe_{0.90}$ and $Li_2PdCl_4 + FeCl_3GH_2O$ using the band of 754 cm⁻¹, (d) catalyzed by $GO@H-Pd_{0.10}Fe_{0.90}$; ReactIR plots with time for the resultant of Suzuki reaction at 55 °C, (a*) 3D map catalyzed by $GO@H-Pd_{0.10}Fe_{0.90}$, (b*) 3D map catalyzed by $Li_2PdCl_4 + FeCl_3GH_2O$, (c*) Kinetic analysis of catalytic reaction of $GO@H-Pd_{0.10}Fe_{0.90}$ and $Li_2PdCl_4 + FeCl_3GH_2O$ using the band of 754 cm⁻¹, (d*) catalyzed by $Li_2PdCl_4 + FeCl_3GH_2O$, (c*) Kinetic analysis of catalytic reaction of $GO@H-Pd_{0.10}Fe_{0.90}$ and $Li_2PdCl_4 + FeCl_3GH_2O$ using the band of 754 cm⁻¹, (d*) catalyzed by $GO@H-Pd_{0.10}Fe_{0.90}$.



Fig. 7. ReactIR plots with time for the resultant of Suzuki reaction (a) 3D map catalyzed by Li₂PdCl₄ + FeCl₃·6H₂O at 70 °C, (b) Kinetic analysis of catalytic reaction of **GO@H-Pd**_{0.10}**Fe**_{0.90} and Li₂PdCl₄ + FeCl₃·6H₂O at 70 °C (a*) 3D map catalyzed by Li₂PdCl₄ + FeCl₃·6H₂O at 70 °C (a*) 3D map catalyzed by Li₂PdCl₄ + FeCl₃·6H₂O at 55 °C, (b*) Kinetic analysis of catalytic reaction of **GO@H-Pd**_{0.10}**Fe**_{0.90} and Li₂PdCl₄ + FeCl₃·6H₂O at 70 °C (a*) 3D map catalyzed by Li₂PdCl₄ + FeCl₃·6H₂O at 55 °C, (b*) Kinetic analysis of catalytic reaction of **GO@H-Pd**_{0.10}**Fe**_{0.90} and Li₂PdCl₄ + FeCl₃·6H₂O using the band of 754 cm⁻¹ at 55 °C (c*) catalyzed by Li₂PdCl₄ + FeCl₃·6H₂O at 55 °C.

3.4. Investigation on the catalytic mechanism

3.4.1. Hot filtration and poison test

How to distinguish homo- or heterogeneous catalyst is an important research [54]. The yield went up rapidly before 40 min, then increased slowly and completed with 95% yield after 90 min (Figure S18). The high efficiency of **GO@H-Pd**_{0.10}**Fe**_{0.90} catalyst could be attributed to the favorable dispersibility in solution with the help of **GO**. To confirm whether there were metals leaching during catalytic process, **GO@H-Pd**_{0.10}**Fe**_{0.90} catalyst was removed after 30 min and then the kinetics was detected till 90 min. The yield did not increase and remain the constant (57–59%) (Figure S18 (red line)). It was the evident that few leaching of catalyst occurred during the catalytic process [54].

To further ensure whether or not catalysis was heterogeneous and where the catalytic reaction occurred, poison experiment was carried out (Table S2). When a little mercury was put into the mixture before starting, catalytic activity could not efficient be inhibited as mercury could not completely cover the active centre on the surface due to its poor dispersibility. The activity of the catalyst was obviously decreased with the addition of 2'2-Dipyridyl. So, 2'2-Dipyridyl was an effective poisoning additive even at less 1.0 equiv than metal atom, indicating that catalytic active centre was on the surface of **GO@H-Pd_{0.10}Fe_{0.90}** monolayer which was characteristic property of heterogeneous catalyst [65].

3.4.2. Electrochemical impedance spectra (EIS) tests

Furthermore, by means of EIS, the impedance's variation of the process of reaction was studied (Figure S19). In high frequency area, the change of diameter of the EIS showed firstly decreases, and then increases trend during the reaction process. It was predicted that the decreases in 1 h was due to Pd (II) were reduced to Pd⁰, and the metal particles could enhance electrical conductivity and facilitate the transfer of charge. Subsequently, the increases in 2 h indicated that the

capability of electrical conductivity was declined. The reason was that as the reaction time increases, the amount of Pd⁰ increases and there was a small amount of aggregation, and wasn't conducive to conduction and charge transfer. The results showed that appropriate number of Pd⁰ was conducive to the catalysis.

3.4.3. Studies on the formation of catalytic active centre

The delivery of various elements at different time and recycled catalysts were obtained by XPS in order to investigate what the real active centre was during catalytic process. For GO@H-Pd_{0.10}Fe_{0.90} in which the palladium was a major Pd (II) species, a pair of Pd 3d peaks at 340.59 and 335.25 eV corresponded to Pd⁰ were observed in 1 h (Fig. 5a), suggesting that Pd^0 might be the real active centre. However, the binding energy of Fe³⁺ shifted to high binding energy during catalysis and recycling process compared with that of fresh catalyst (Fig. 5b), indicating that electron might transfer from Fe to Pd occurred due to the cooperation between Pd and Fe. It was proposed that GO transferred electron to Fe via ligand, then to Pd via Fe, which made active Pd more negative which was easy for oxide addition. It also gave an evident that the catalytic activity could be promoted by not only single metal, but Pd/Fe system in proper manner. Impressively, B 1 s and Br 3p were detected at 1 h, 2 h and cycle 4th runs of the reaction (Fig. 5c).

Another fascinating question is how Fe interacts with Pd in GO@H-Pd_{0.10}/Fe_{0.90} to yield higher activity. It can be proposed that Fe³⁺ can increased the valence of Pd by injecting electrons into Pd²⁺. According to the result of DFT, Pd⁰ was easily to form the oxidation insertion intermediate. The bond length of Pd-C, Pd-Br, and C-Br are 2.77, 2.61, and 2.02 Å in TS, and the oxidative insertion EB is 5.6 kcal/mol (Figure S20). In addition, there were no results were calculated using Fe and Pd (II) as active centre. We also obtained the oxidation potential E of complexes (Figure S21), and the results showed that electrons were found to be penetrating from Fe to Pd when the R1 as the ligand. As



Fig. 8. ReactIR plots with time for the resultant of Suzuki reaction (a) 3D map catalyzed by $Li_2PdCl_4 + FeCl_3 \cdot 6H_2O + GO$ at 70 °C (b) catalyzed by $Li_2PdCl_4 + FeCl_3 \cdot 6H_2O + GO$ at 70 °C, (a*) 3D map catalyzed by $Li_2PdCl_4 + FeCl_3 \cdot 6H_2O + GO$ at 70 °C, (a*) 3D map catalyzed by $Li_2PdCl_4 + FeCl_3 \cdot 6H_2O + GO$ at 70 °C, (a*) 3D map catalyzed by $Li_2PdCl_4 + FeCl_3 \cdot 6H_2O + GO$ at 70 °C, (a*) 3D map catalyzed by $Li_2PdCl_4 + FeCl_3 \cdot 6H_2O + GO$ at 70 °C, (a*) 3D map catalyzed by $Li_2PdCl_4 + FeCl_3 \cdot 6H_2O + GO$ at 70 °C, (a*) 3D map catalyzed by $Li_2PdCl_4 + FeCl_3 \cdot 6H_2O + GO$ at 70 °C, (a*) 3D map catalyzed by $Li_2PdCl_4 + FeCl_3 \cdot 6H_2O + GO$ at 70 °C, (b*) catalyzed by $Li_2PdCl_4 + FeCl_3 \cdot 6H_2O + GO$ at 70 °C, (b*) catalyzed by $Li_2PdCl_4 + FeCl_3 \cdot 6H_2O + GO$ at 70 °C, (b*) catalyzed by $Li_2PdCl_4 + FeCl_3 \cdot 6H_2O + GO$ at 70 °C, (b*) catalyzed by $Li_2PdCl_4 + FeCl_3 \cdot 6H_2O + GO$ at 70 °C, (b*) catalyzed by $Li_2PdCl_4 + FeCl_3 \cdot 6H_2O + GO$ at 70 °C, (b*) catalyzed by $Li_2PdCl_4 + FeCl_3 \cdot 6H_2O + GO$ at 70 °C, (b*) catalyzed by $Li_2PdCl_4 + FeCl_3 \cdot 6H_2O + GO$ at 70 °C, (b*) catalyzed by $Li_2PdCl_4 + FeCl_3 \cdot 6H_2O + GO$ at 70 °C, (b*) catalyzed by $Li_2PdCl_4 + FeCl_3 \cdot 6H_2O + GO$ at 70 °C, (b*) catalyzed by $Li_2PdCl_4 + FeCl_3 \cdot 6H_2O + GO$ at 70 °C, (b*) catalyzed by $Li_2PdCl_4 + FeCl_3 \cdot 6H_2O + GO$ at 70 °C, (b*) catalyzed by $Li_2PdCl_4 + FeCl_3 \cdot 6H_2O + GO$ at 70 °C, (b*) catalyzed by $Li_2PdCl_4 + FeCl_3 \cdot 6H_2O + GO$ at 70 °C, (b*) catalyzed by $Li_2PdCl_4 + FeCl_3 \cdot 6H_2O + GO$ at 70 °C, (b*) catalyzed by $Li_2PdCl_4 + FeCl_3 \cdot 6H_2O + GO$ at 70 °C, (b*) catalyzed by $Li_2PdCl_4 + FeCl_3 \cdot 6H_2O + GO$ at 70 °C, (b*) catalyzed by $Li_2PdCl_4 + FeCl_3 \cdot 6H_2O + GO$ at 70 °C, (b*) catalyzed by $Li_2PdCl_4 + FeCl_3 \cdot 6H_2O + GO$ at 70 °C, (b*) catalyzed by $Li_2PdCl_4 + FeCl_3 \cdot 6H_2O + GO$ at 70 °C, (b*) catalyzed by $Li_2PdCl_4 + FeCl_3 \cdot 6H_2O + GO$ at 70 °C, (b*) catalyzed by $Li_2PdCl_4 + FeCl_3 \cdot 6H_2O + GO$ at 70 °C, (b*) catalyzed by $Li_2PdCl_4 +$

mentioned above, with which electrons might be penetrating into Pd via Fe. As mentioned above, we thought the active system containing Pd^{2+} , Pd^0 and Fe^{3+} would be the real catalytic active centre It was speculated that this might be due to the formation of intermediates between substrate and metal within or on the surface of the catalyst during the reaction. Speculated electron transfer in the catalytic process was shown in Fig. 5c based on the experimental data (Scheme 2).

ReactIR was usually used for investigating on the catalytic process [66,67]. While in the prophase of heterogeneous catalysis, there was adsorption between substrate and catalyst, which was similar to the induction period described above [68,69]. So the existence of "induction period" and the sigmoidal shaped curve can be used as a way to distinguish heterogeneous from homogeneous the catalytic process.

ReactIR catalyzed by GO@H-Pd_{0.10}Fe_{0.90} and Li₂PdCl₄/FeCl₃·6H₂O showed marked difference catalytic process (Fig. 6). For GO@H-Pd_{0.10}Fe_{0.90}, the peak intensity presented an increasing trend with increasing time. First, there was an "induction period" with almost no product, then the peak intensity increased with increasing time (Fig. 6c, red line). Its phenomenon was the characteristic of heterogeneous catalytic process. However, Li₂PdCl₄/FeCl₃·6H₂O (Fig. 6b) showed completely different phenomena that the intensity of peak did not change during the recording time. The marked difference changes indicated different catalytic mechanism catalyzed by GO@H-Pd_{0.10}Fe_{0.90} and Li₂PdCl₄/FeCl₃·6H₂O. The results of the plots at 754 cm⁻¹ for Li₂PdCl₄/FeCl₃·6H₂O showed different in Fig. 6c. According to the results of GO@H-Pd_{0.10}Fe_{0.90} and the presence of sigmoidal kinetics [70], the heterogeneous surface catalytic mechanism could be confirmed, including surface absorption, intermediates forming by reacting with active centre, diffusion, yielding product, desorption and recovery.

Although Li₂PdCl₄/FeCl₃·6H₂O could be evenly dispersed in solution, it doesn't catalyze very well at the limited amount. It was also an important evident that ordered **GO@H-Pd_{0.10}/Fe_{0.90}** had higher activity than that of Li₂PdCl₄/FeCl₃·6H₂O under the same condition. The similar result was also obtained even at lower temperature as shown in Fig. 6a*-c*. The rate constants (70 °C, $k_1 = 0.0325$; 55 °C, $k_2 = 0.0278$) and apparent activation energy (E_{a Hetero} = 9.7 KJ/mol) were obtained according to the kinetic curves under different reaction conditions (Fig. 6d and Fig. 6d*).

In order to investigate the dynamics of homogeneous and heterogeneous catalyst, experiments were designed with different temperature, with which the activation energy of two catalysts according to the kinetic curves were calculated (Fig. 7). The catalytic activity of homogeneous catalysts with the same amount of **GO@H-Pd**_{0.10}**Fe**_{0.90} was very low. Thus, the amount of homogeneous catalysts used was as 40 times as more as that of heterogeneous catalyst. The experimental data showed that the catalytic rate was higher than that of heterogeneous catalysts (Fig. 7b and Fig. 7b*). The reaction rate constants (70 °C, $k_1 = 0.00615$; 55 °C, $k_2 = 0.0058$) and apparent activation energy (E_a Homo = 3.7 KJ/mol) were obtained according to the kinetic curves under different reaction conditions. Different catalytic mechanism could be confirmed by the dynamic data obtained above.

It was contrary since that the $E_{a \text{ Hetreo}}$ was larger than that of $E_{a \text{ Homo}}$ presented. Considering surface catalytic mechanism for **GO@H-Pd**_{0.10}**Fe**_{0.90}, effect of solid particles on the heterogeneous reaction system must be investigated. In order to eliminate this effect, the same amount of **GO** or carbon powder (**CP**) was added into the homogeneous catalytic system. The results were as follow: the reaction rate constants (70 °C, $k_1 = 0.0018$; 55 °C, $k_2 = 0.00132$) and apparent activation



Fig. 9. ReactIR plots with time for the resultant of Suzuki reaction (a) 3D map catalyzed by $\text{Li}_2\text{PdCl}_4 + \text{Fecl}_36\text{H}_2\text{O} + \mathbf{CP}$ at 70 °C (b) catalyzed by $\text{Li}_2\text{PdCl}_4 + \text{Fecl}_36\text{H}_2\text{O} + \mathbf{CP}$ at 70 °C (a*) 3D map catalyzed by $\text{Li}_2\text{PdCl}_4 + \text{Fecl}_36\text{H}_2\text{O} + \mathbf{CP}$ at 55 °C, (b*) catalyzed by $\text{Li}_2\text{PdCl}_4 + \text{Fecl}_36\text{H}_2\text{O} + \mathbf{CP}$ at 55 °C.



Scheme 3. Supposed plausible catalytic pathway.

energy (E_{a Homo} = 19.3 KJ/mol) were obtained according to the kinetic curves under the addition of **GO** (Fig. 8). The reaction rate constants (70 °C, $k_1 = 0.00218$; 55 °C, $k_2 = 0.00146$) and apparent activation energy (E_{a Homo} = 25.0 KJ/mol) were obtained according to the kinetic curves under the addition of **CP** (Fig. 9). Experimental results showed that the solid support had effect on the catalytic activity of catalyst, and revealed that heterogeneous catalysts have high catalytic activity and could greatly reduce the activation energy required for the reaction.

From the results above, heterogeneous catalytic process could be proposed, in which active centre formation, absorption of substrate, forming intermediates via active centre, target molecular formation and desorption of product from the surface occurred (Scheme 3). The process could be described as that: At the beginning of the reaction, under the action of a base, the conversion of bivalent palladium to zero valent palladium through electron transfer between ligand, support and metals. The substrate was first absorbed on the surface, then contact to the catalytic activity site to form intermediates through oxidative addition. Subsequently, the intermediate reacted with phenyl boron acid and transferred into products through metal transition and reductive elimination. Finally, the product diffused into the solution.

4. Conclusions

Pd (II)/Fe (III) bimetallic catalytic monolayer supported on GO (denoted as GO@H-Pd/Fe) was fabricated and its catalytic properties, synergetic effect and catalytic mechanism were systematic investigated. Results showed that composition and orientation of catalyst had effect on enhancing catalytic activity. Catalytic activity of GO@H-Pd_{0.10}/ Fe0.90 was 475 times more than that of GO@H-Pd due to the synergetic effect between Pd and Fe, from which GO transferred electron to Fe (III) via ligand, then to Pd, which made active Pd more negative. It played a great role for promoting catalytic activity since it was easy for oxide addition. GO@H-Pd/Fe exhibited better stability and recyclability at least 8 times due to proper functional ligand and support. Deactivation mechanism was confirmed to be the aggregation of active centre and the loss of catalyst during the recycling. Heterogeneous catalysis was also proved, in which the catalytic reaction occurred on the surface. Dynamic studies were deeply investigated by ReactIR. The results presented different catalytic process for GO@H-Pd_{0.10}Fe_{0.90} and homogeneous catalyst. The activation energies were 9.7 KJ/mol and 3.7 KJ/mol for heterogeneous and homogeneous catalyst, respectively. The inference factor of supports on the results in ReactIR for calculating activation energy was also investigated, with which that GO@H- $Pd_{0.10}Fe_{0.90}$ catalytic activity was higher than that of homogeneous catalyst could be confirmed.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2019.03.004.

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