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***N*-heterocyclic carbene palladium complex supported on ionic liquid-modified graphene oxide as an efficient and recyclable catalyst for Suzuki reaction**

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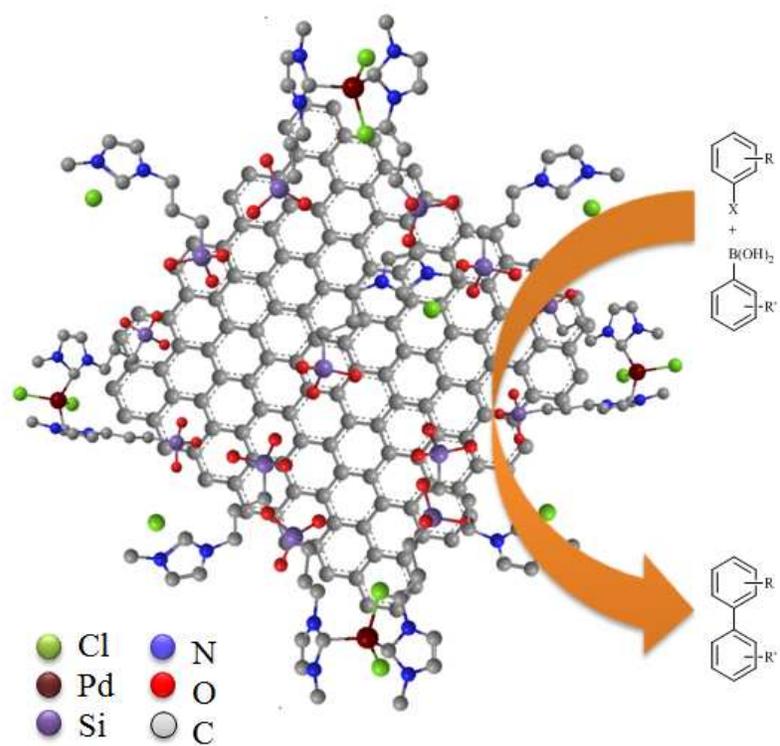
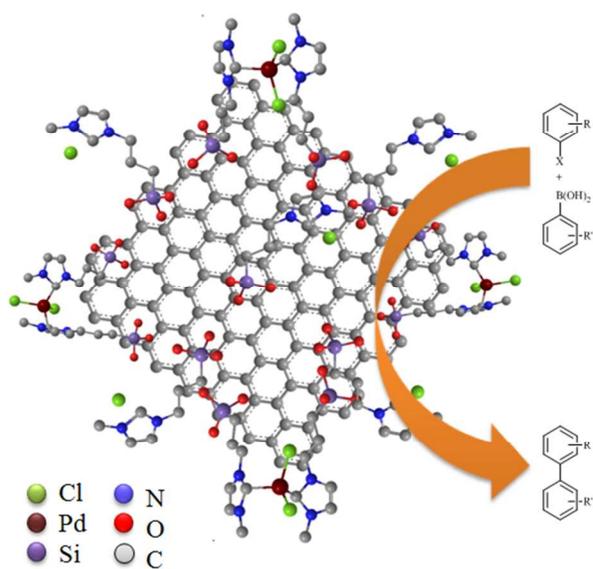


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ARTICLE TYPE

N-heterocyclic carbene palladium complex supported on ionic liquid-modified graphene oxide as an efficient and recyclable catalyst for Suzuki reaction

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N-heterocyclic carbene palladium complex immobilized on graphene oxide (GO) with ionic liquid framework (NHC-Pd/GO-IL) was synthesized by the modification of GO through silylation reaction. The obtained catalyst displayed a high activity toward Suzuki reaction in EtOH/H₂O (1:1).

The interest in ionic liquids (ILs) has increased dramatically in the past decade as their unique properties such as low vapour pressure, low toxicity, high chemical and thermal stabilities, and wide liquid range and favourable solvating properties.¹ Mehnert has described the concept of supported ionic liquid catalysis, which involves the treatment of a monolayer of covalently attached ionic liquid on the surface of silica gel with additional ionic liquid.² These layers serve as the reaction phase in which the homogeneous catalyst is dissolved. When ionic-liquid-supported (ILS) catalysts are used for organic reactions that are carried out in a homogeneous system, they may have similar or even higher catalytic activity and selectivity, compared to the homogeneous parent catalyst system. The active species-although the resulting material is a solid-is dissolved in the ionic liquid and act like a homogeneous catalyst.³ Several studies have successfully confined various ionic liquid phases to the surface of different supports and applied them in some catalytic processes.⁴

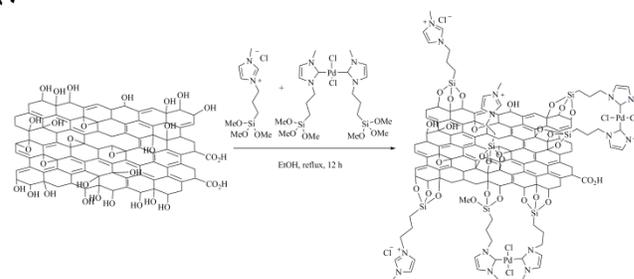
Recently, graphene which is a single layer of sp² carbon atoms bonded in a hexagonal lattice has attracted high attention of scientists all over the world. The extraordinary properties of the exfoliated graphene sheets, such as their extremely large surface area,⁵ fast charge mobility,⁶ remarkably high mechanical strength and Young's modulus,⁷ excellent chemical stability⁸ and low manufacturing cost make graphene as promising candidate to disperse or immobilize catalytically active species for heterogeneous catalysis.⁹ Recently, the silylation modification technique on graphene oxide has been reported and can provide graphene nanocomposites with catalytic activities.¹⁰

Aryl-aryl bond formation *via* palladium-catalyzed Suzuki cross coupling reaction is one of the most important tools of modern organic synthesis. The Suzuki cross coupling reaction is one of the most general and powerful tools for the synthesis of pharmaceuticals, herbicides, polymers, liquid crystals, natural products, ligands for catalysis and advanced materials.¹¹

Herein, we report a novel protocol for the Suzuki cross coupling catalyzed by *N*-heterocyclic carbene palladium complex

immobilized on GO with ionic liquid framework (NHC-Pd/GO-IL). Additionally, the effects of solvent polarity, base, and temperature on yield, and recycling potential of the catalyst have all been assessed.

The process for the preparation of NHC-Pd/GO-IL nanocomposite is schematically described in Scheme 1. First, the reaction of sub-stoichiometric amount of Pd(OAc)₂ with an excess of imidazolium ionic liquid (IL) afforded *N*-heterocyclic carbene palladium complex (NHC-Pd)-imidazolium ionic liquid (IL). In order to graft the NHC-Pd-IL on the surface graphene oxide, the reaction of NHC-Pd complex in IL and graphene oxide carried out in EtOH under reflux conditions for 12h.



Scheme 1 Schematic description for preparation of NHC-Pd/GO-IL

NHC-Pd/GO-IL nanocomposite was characterized by FT-IR, SEM, TEM, Raman, XPS, TGA and EDS mapping measurements. FT-IR spectra of GO and NHC-Pd/GO-IL nanocomposite are shown in (Fig. 1). In the spectrum of GO, strong absorption bands at 1732, 1068 and 3428 cm⁻¹ correspond to stretching vibration of C=O, C-O (epoxy) and O-H, respectively. The peaks at 1623 and 1286 cm⁻¹ correspond to the vibration of carboxyl groups.¹² The FT-IR spectrum of NHC-Pd/GO-IL, exhibited new three peaks around 1567, 1036 and 751 cm⁻¹, compared with the FT-IR spectroscopy of GO. These peaks corresponded to the ring vibration of the imidazole,¹³ and stretching vibrations of Si-O and Si-O-C, respectively, and provide direct evidences for the successful silylation of GO.¹⁴

A scanning electron microscopy (SEM) image of the GO displayed two-dimensional structures with crumpling feature (Fig. 2a). The density and distribution of the NHC-Pd and IL groups on the NHC-Pd/GO-IL nanocomposite are evaluated by quantitative energy dispersive X-ray spectroscopy (EDS) mapping. As can be seen in Fig. 2b-d, rather than only located at

the edges of graphene sheets, the elements N, Pd and Si are found to be uniformly dispersed on the whole surface of NHC-Pd/GO-IL nanocomposite indicating the homogeneous distribution of the NHC-Pd and IL groups.

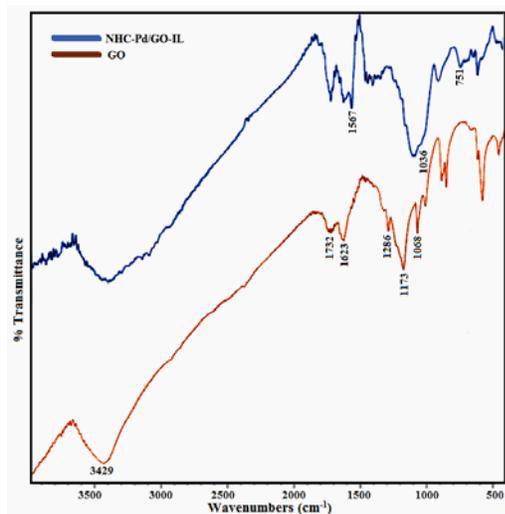


Fig. 1 FTIR spectra of GO and NHC-Pd/GO-IL nanocomposite

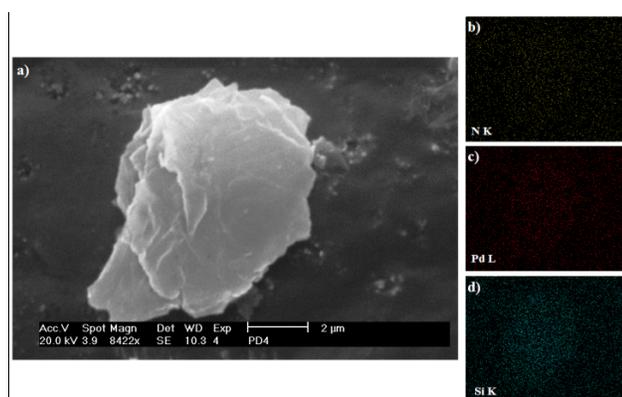


Fig. 2 SEM image of (a) NHC-Pd/GO-IL, and corresponding quantitative EDS element mapping of (b) N, (c) Pd and (d) Si.

Raman spectra of GO and NHC-Pd/GO-IL (Fig. 3) show an obvious blue shift of the G band from 1588.52 to 1594.83 cm^{-1} , probably due to the gradually increased compressive local stress induced by the attached NHC-Pd and IL on the surface of graphene oxide.¹⁵

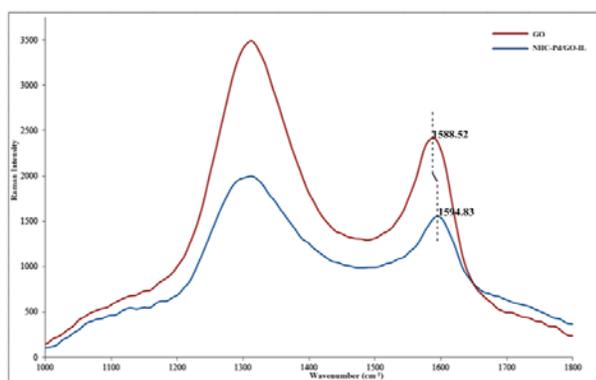


Fig. 3 Raman spectra of GO and NHC-Pd/GO-IL nanocomposite

The electronic properties of nanocomposite were probed by X-ray photoelectron spectroscopy (XPS) analysis. As shown in Fig. 4, the peaks corresponding to Cl 2p & 2s, N 1s, Pd 3s & 3p & 3d, and Si 2s & 2p can be clearly observed in the XPS full spectrum. A pronounced peak at 101.9 eV (in Si 2p XPS spectrum) which corresponds to the bonding energy of Si–O–C can be easily observed. The N 1s spectra could be divided into two peaks, one peak at 399.2 eV ascribed to sp^2 nitrogen in aromatic ring of NHC-Pd(II) complex and another 401.2 eV peak attributed to the quaternary nitrogen of IL.¹⁶ By integrating the area in the XPS has been found the ratio of sp^2 nitrogen : quaternary nitrogen to be 1:9 that supported with hypothetical for preparation of the catalyst NHC-Pd/GO-IL nanocomposite. The XPS spectrum of Pd 3d core level region for NHC-Pd/GO-IL nanocomposite displays main peaks at 337.7 and 342.9 eV which can be attributed to the binding energy of Pd $3d_{5/2}$ and Pd $3d_{3/2}$, respectively. These values correspond to the Pd(II) binding energy of NHC-Pd(II) complex. Additionally, The formation of the NHC-Pd complex was confirmed that the Pd $3d_{5/2}$ binding energy values changed from 338.8 eV to 337.7 eV after the ionic liquid was reacted with $\text{Pd}(\text{OAc})_2$.¹³

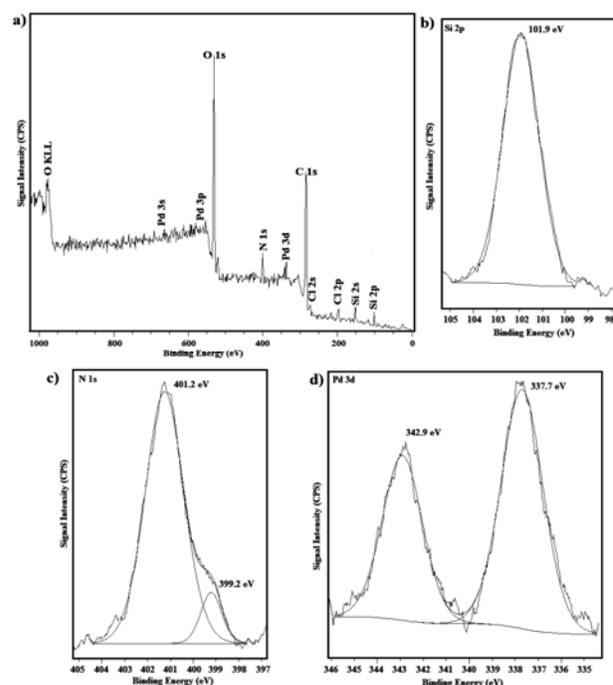


Fig. 4 Full range XPS spectrum (a), and the Si 2p (b), N 1s (c), Pd 3d (d) core level regions XPS spectra of NHC-Pd/GO-IL nanocomposite, respectively.

Thermo gravimetric analysis (TGA) was further used to study the composition of NHC-Pd/GO-IL nanocomposite. TGA plots of GO and NHC-Pd/GO-IL nanocomposite are shown in Fig. 5. In the GO, the weight lost was about 57.7% at temperatures below 154°C, due to pyrolysis of the labile oxygen-containing functional groups. In contrast, the NHC-Pd/GO-IL nanocomposite showed good thermal stability. The total weight lost was only 6.8% at temperatures below 169 °C.

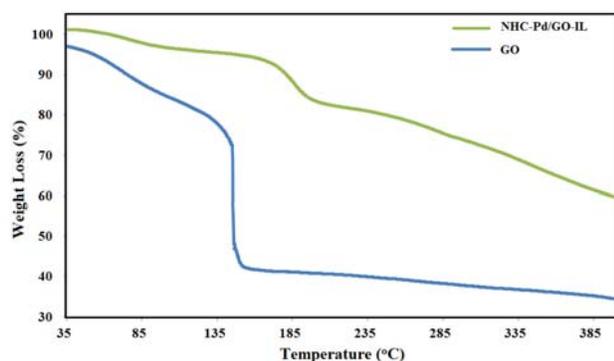


Fig.5 TGA plots of GO and NHC-Pd/GO-IL nanocomposite.

The catalytic activity of the NHC-Pd/GO-IL nanocomposite as precatalyst was then tested in Suzuki reaction. To optimize the reaction conditions, phenyl boronic acid and phenyl iodide were selected as model substrates in the presence of various bases and solvents (Table 1). By using H₂O as the solvent, the reaction was tested employing various bases such as K₂CO₃, Et₃N, K₃PO₄, and KOH at 60 °C (Table 1, entries 1-4). A superior yield obtained when K₂CO₃ was used as the base (Table 1, entry 1). Then, different solvent such as EtOH, MeOH, CH₂Cl₂, CH₃CN and EtOH/H₂O (1:1) were screened in the model reaction using K₂CO₃ as base (Table 1, entries 5-9). It was found that the reaction using EtOH/H₂O (1:1) after 2.5 h resulted in higher yield. The Effect of the NHC-Pd/GO-IL loading was also investigated under the optimum reaction conditions (Table 1, entries 5, 10 and 11). It was found that when the amount of the NHC-Pd/GO-IL increased from 0.02 to 0.05, and 0.1 mol %, the yields increased from 42, 58 to 98%, respectively. It was found that 0.1 mol% NHC-Pd/GO-IL is sufficient to push this reaction forward (Table 1, entry 5). To optimize the reaction temperature, we also performed several experiments at 50 °C, 60 °C and 70 °C in the presence of K₂CO₃ in EtOH/H₂O (1:1) using 0.1 mol % NHC-Pd/GO-IL (Table 1, entries 5, 12 and 13). As can be seen from Table 1, the most suitable reaction temperature is 60 °C.

Table 1. Screening of the reaction conditions^a

Entry	Solvent	Base	Temp (°C)	Yield (%)
1	H ₂ O	K ₂ CO ₃	60	76%
2	H ₂ O	Et ₃ N	60	Trace
3	H ₂ O	K ₃ PO ₄	60	15%
4	H ₂ O	KOH	60	36%
5	H ₂ O/EtOH (1:1)	K ₂ CO ₃	60	98%
6	EtOH	K ₂ CO ₃	60	64%
7	MeOH	K ₂ CO ₃	60	22%
8	CH ₂ Cl ₂	K ₂ CO ₃	reflux	Trace
9	CH ₃ CN	K ₂ CO ₃	60	Trace
10 ^b	H ₂ O/EtOH (1:1)	K ₂ CO ₃	60	42%
11 ^c	H ₂ O/EtOH (1:1)	K ₂ CO ₃	60	58%
12	H ₂ O/EtOH (1:1)	K ₂ CO ₃	50	81%
13	H ₂ O/EtOH (1:1)	K ₂ CO ₃	70	98%

^aPhenyl iodide (1.0 mmol), phenyl boronic acid (1.3 mmol), Base (3.0 mmol), NHC-Pd/GO-IL (0.1 mol% Pd), 60°C, 2.5 h and solvent (2 ml). GC yield, *n*-dodecane was used as an internal standard. ^bCatalyst (0.02 mol% Pd). ^cCatalyst (0.05 mol% Pd).

With the optimized reaction conditions in hand, we next managed to examine the scope and limitation of Suzuki reaction

with various types of iodo-, bromo-, and chloroaryl derivatives and arylboronic acids (Table 2).

Table 2. NHC-Pd/GO-IL nanocomposite catalyzed Suzuki reaction^a

Entry	Aryl Halide	Aryl boronic acid	Product	Yield ^b
1				98%
2				98%
3				98%
4				82%
5				61%
6				98%
7				92%
8				85%
9				94%
10				98%
11				93%
12 ^b				42%
13 ^b				57%
14 ^b				69%
15 ^b				74%

^aReaction Conditions: Aryl halide (1.0 mmol), aryl boronic acid (1.3 mmol), K₂CO₃ (3.0 mmol), NHC-Pd/GO-IL (0.1 mol% Pd), 60°C, 2.5 h and EtOH/H₂O (1:1) (2 ml). ^b Isolated yield by column chromatography. ^c TBAB (1 mmol), Catalyst (0.2 mol% Pd) and 90°C, 12 h

It can be seen from Table 2 that Suzuki reaction with most substrates proceeded in good yields. Aryl bromides and iodides bearing electron-donating and electron-withdrawing groups reacted well and giving good yields. The hindered substrate such as 2-iodo-1,3,5-trimethylbenzene converted to the corresponding product with a moderate yield (Table 2, entry 5). Unfortunately, the catalytic system was less effective for the reaction of aryl

chlorides and moderate yields was obtained in the presence of tetra butyl ammonium bromide (TBAB) (Table 2, entries 13-15).

The reusability of the NHC-Pd/GO-IL nanocomposite was examined in the Suzuki reaction of phenyl boronic acid with phenyl iodide. It was found that the recovery can be successfully achieved in five successive reaction runs (Table 3).

Table 3. Reusability of the NHC-Pd/GO-IL nanocomposite in Suzuki reaction of phenyl boronic acid with phenyl iodide^a

Reaction cycle	1st	2nd	3rd	4th	5th
Yield ^b (%)	98	97	95	92	90

^aPhenyl iodide (1.0 mmol), phenyl boronic acid (1.3 mmol), K₂CO₃ (3.0 mmol), NHC-Pd/GO-IL (0.1 mol% Pd), 60°C, 2.5 h and EtOH/H₂O (1:1) (2 mL)

^b GC yield, *n*-dodecane was used as an internal standard.

The heterogeneous nature of the precatalysis was proved using a hot filtration test and AAS analysis. To determine whether the catalyst is actually functioning in a heterogeneous manner or whether it is merely a reservoir for more active soluble palladium species, we performed a hot filtration test in the Suzuki reaction of phenyl boronic acid with phenyl iodide after ~50% of the coupling reaction is completed. The hot filtrates were then transformed to another flask containing K₂CO₃ (3 equiv.) in EtOH/H₂O (1:1) at 60 °C. Upon the further heating of catalyst-free solution for 3 h, no considerable progress (~5% by GC analysis) was observed. Moreover, using AAS of the same reaction solution at the midpoint of completion indicated that no significant quantities of palladium are lost to the reaction liquors during the process.

A TEM image of the fresh NHC-Pd/GO-IL nanocomposite displays a crumpled and layer like structure without any nanoparticles (Fig. 6a). As shown in Fig. 6b-c, well distributed fine Pd nanoparticles (Pd NPs) with sizes of less 5 nm dispersed on the GO-IL sheets can be observed after one and three runs in recycled NHC-Pd/GO-IL nanocomposite. This is in an agreement with the previous reported results that the formation Pd nanoparticles as active species were evolved during the catalytic reaction. The formation of Pd nanoparticles during the Suzuki reaction are supposed to be due to the reduction of Pd(II) by phenyl boronic acid.²¹ To demonstrate this assumption, TEM images after experiments without boronic acid (PhI and K₂CO₃) and without all reagents (only the K₂CO₃) show that the Pd nanoparticles are not formed during these experiments (Fig. S1a-b, ESI†).

The imidazolium IL plays an important role in improving the dispersibility of Pd NPs and preventing the aggregation or agglomeration of Pd NPs on the GO-IL sheets.¹⁷ Additionally, Pd NPs are not found outside of the GO-IL sheets.

Table 4, compares efficiency of NHC-Pd/GO-IL nanocomposite (time, yield, reaction conditions) with efficiency of other reported heterogeneous palladium catalysts in Suzuki reaction. It is clear from Table 4 that our method is simpler, more efficient, and less time consuming for Suzuki reaction.

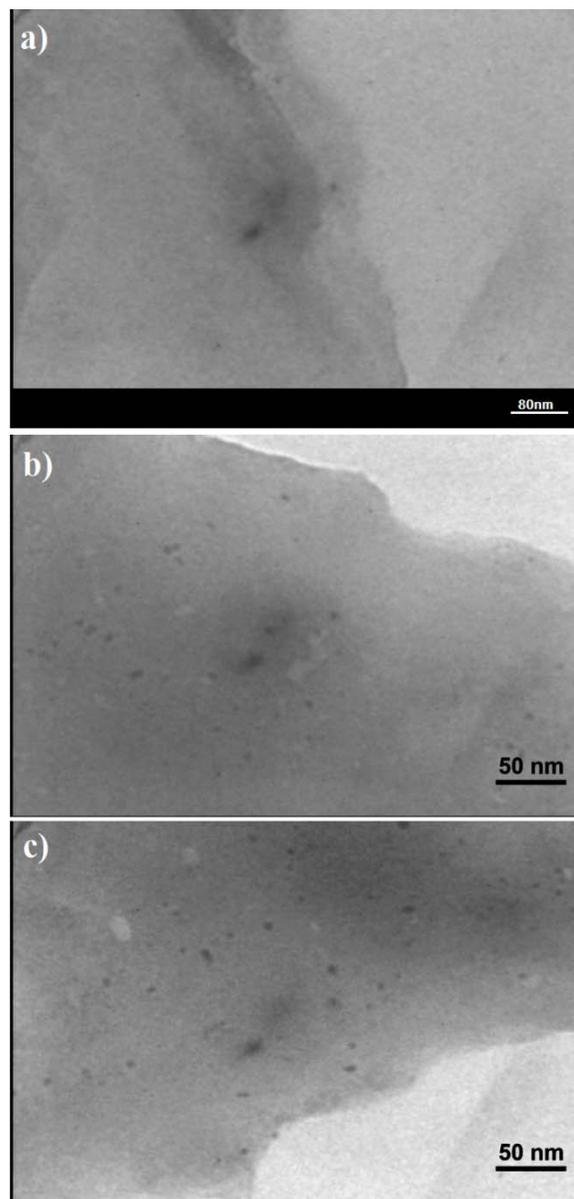


Fig. 6 TEM images of (a) the fresh NHC-Pd/GO-IL nanocomposite, (b) the NHC-Pd/GO-IL reused after one run and (c) the NHC-Pd/GO-IL reused after three run

Table 4. Comparison of efficiency of various heterogeneous palladium catalysts in Suzuki reaction

Catalyst	Condition	Yield	Time	Ref.
NHC-Pd/GO-IL (0.1-0.2 mol%)	K ₂ CO ₃ , EtOH/H ₂ O (1:1), 60-90 °C	42-98(%)	2.5-12 h	This work
NHC-Pd/SBA-16-IL (0.01 mol%)	K ₃ PO ₄ , EtOH/H ₂ O (1:1), 50 °C	87-99 (%)	5-10 h	13
GO-NHC-Pd ²⁺ (0.25 mol%)	K ₂ CO ₃ , EtOH/H ₂ O (1:1), 80 °C	23-96 (%)	1-24 h	17
MPS-NHC-Pd (1-2 mol%)	K ₂ CO ₃ , DMF/H ₂ O (2:1), 50-100 °C	31-99 (%)	0.5-24 h	18
Pd@PMO-IL (0.1-1 mol%)	K ₂ CO ₃ , H ₂ O, 60-90 °C	60-99 (%)	2-20 h	19
Pd NPs-IP-IL (1 mol%)	Na ₂ CO ₃ , H ₂ O, 100 °C	6-99 (%)	2.5-10 h	20

Conclusions

We have demonstrated for the first time that an ionic liquid based graphene by grafting the *N*-heterocyclic carbene palladium complex on the surface of the graphene oxide modified with ionic liquids is an effective and powerful support for the immobilization and stabilization of Pd nanoparticles on the Suzuki reaction. The nanocomposite shows good catalytic activity for the Suzuki coupling of a variety of activated and deactivated aryl halides with aryl boronic acids. Leaching tests such as hot filtration test and AAS analysis indicate that the catalytic reaction is mainly heterogeneous in nature. The reusability of this catalyst is high and the catalyst can be reused several times without significant decrease in its catalytic activity. Furthermore, the TEM image of the recovered catalyst showed the presence of well-distributed Pd NPs on the GO-IL sheets without any aggregation. Further applications of the catalytic system in other palladium catalyzed reactions are under investigation in our laboratory.

Notes and references

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- † Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/
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