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ARTICLE TYPE

Design and synthesis of a new functionalized-clay composite for stabilization of palladium nanoparticles. Application as a recoverable catalyst for C-C bond formation reactions

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A new clay composite carrying phosphinite-functionalized ionic liquid moieties (CCPIL) has been designed and synthesized. Palladium nanoparticles were ligated by CCPIL uniformly. After characterization, this composite has been applied as a heterogeneous catalyst for Suzuki-Miyaura reaction of aryl halides with phenylboronic acid in the presence of NaOH as the base on water. These nanoparticles have also been applied for copper-free Sonogashira-Hagihara reaction in TBAB and Mizoroki-Heck reaction under solvent-free conditions. The catalyst was also found to be stable towards moisture and air and its catalytic activity restored almost completely after three months exposure to the air.

Introduction

In today's economic and industrial vision, using less toxic reaction solvents such as water and ionic liquids are important from green chemistry point of view. In addition, removal of metal wastes from the reaction media and also recovery of expensive metal catalysts are two important subjects to be examined. Along this line, chemists are interested in searching for using ionic liquids (ILs) as novel and green solvents, catalysts and reagents.[1] ILs have special properties, such as non-volatility, non-flammability and a wide temperature range over the liquid phase.[2] They have polarities similar to light alcohols, in which polar organic compounds, gases and biocatalysts are dissolved, and allow the reactions to perform under homogeneous conditions.[3] By considering these facts, replacing organic solvents with ionic liquids in organic reactions would be of a great interest. However, ionic liquids are expensive materials and their use as a solvent is not desirable economically. Nevertheless, by immobilization of ILs onto the surface of a solid support, organic reactions can proceed on the thin IL layer on the surface of the support and minimize the amount of used ILs. In addition, supporting of ionic liquids on inorganic materials facilitates their purification processes, recycling and isolation of the products from the reaction mixtures.[4-6] Incorporation of ionic liquids may be achieved by two approaches; the first approach is their immobilization by covalent binding[4,5] and the second is adsorption of the ILs on the surface of a solid supports.[6]

Clay minerals occur widely in nature and their high surface area and ion exchange properties make it suitable to use as a solid support.[7] A class of clays are Mg-organosilicates containing pendant organic groups. The composition of these organo-functionalized clays has been reported to be $R_8Si_8Mg_6O_{16}(OH)_4$, where R is an organic group.[8]

Transition metals have come to play an important role in metal-catalyzed reactions for creating C-C bonds.[9] One of the most booming protocols for C-C bond formation between two sp^2 carbons is Suzuki-Miyaura reaction in which biaryl compounds are produced.[10] Various palladium nanoparticles have been used as catalysts for the promotion of this reaction[11] and numerous reviews are available in the literature in which the use of palladium nanoparticles in Suzuki-Miyaura reaction have been discussed.[10a,12] Sonogashira-Hagihara reaction which is one of the most successful methods to form substituted alkynes, has been widely applied in the synthesis of natural products, biologically active molecules and different materials.[13] Another palladium catalyzed reaction which also proceeds between two sp^2 carbons is called Mizoroki-Heck reaction. It produces functionalized alkenes that are applied in the synthesis of many organic compounds.[14] Very recently, palladium nanoparticles supported on amine- and phenyl-functionalized clay has been reported to catalyze carbon-carbon bond formation reactions.[15]

In recent years, we have reported the synthesis and application of functionalized ILs,[16a,b] and heterogeneous palladium catalysts for different palladium catalyzed reactions.[16c-f] Now, in this study, we have combined the advantages of homogeneous IL phase, phosphorylated ligands and a new heterogeneous clay support for Pd catalyzed C-C bond formation in green media.
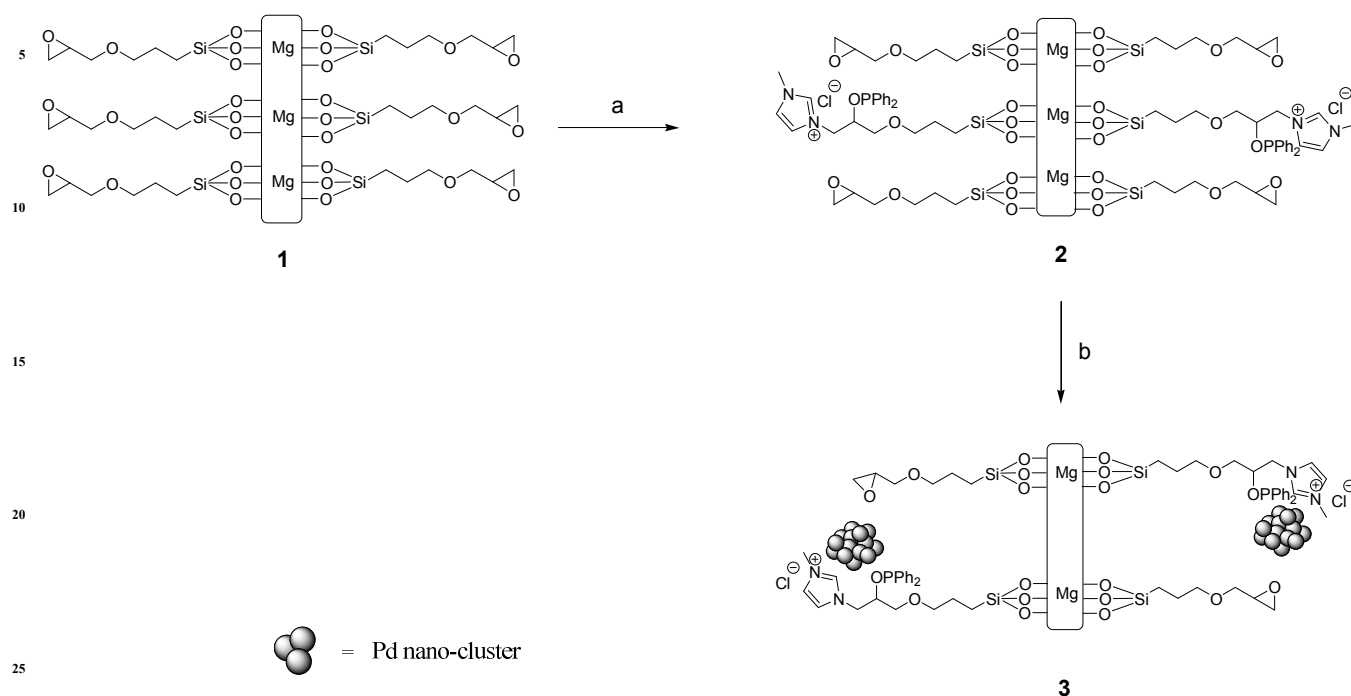
Reaction conditions: (a) 1-Methyl imidazole, Ph$_2$PCl, CH$_2$Cl$_2$, 50 °C, under Ar, 24 h; (b) PdCl$_2$ (aqueous solution), rt, 24 h

Scheme 1. Synthesis of CCPIL and deposition of palladium nanoparticles on it

Results and Discussion

Initially, the epoxy-functionalized clay (**1**) was prepared by the method reported in the literature.[17] In order to build up the ionic moiety on the surface of the clay, the epoxy-functionalized clay was dispersed in CH$_2$Cl$_2$ by sonication. 1-Methyl imidazole was added to the reaction vessel followed by diphenyl phosphine chloride and allowed the reaction to stir at 50 °C for 24 h under argon atmosphere. The resulting clay composite carrying phosphinite-functionalized ionic liquid moietie (CCPIL, **2**) was separated by simple filtration and washed with CH$_2$Cl$_2$ to give the purified organic-inorganic hybrid material (Scheme 1).

FT-IR spectrum of **1** showed bands at 3433 cm^{-1} (Si-OH group) and 565 cm^{-1} (Mg-O absorption) (Figure 1a). FT-IR spectrum of **2** also showed the same bands plus absorption bands for P-O (1071 cm^{-1}), C-O (1138 cm^{-1}) and C=C stretching of aromatic rings (1438 cm^{-1}), confirming that phosphinite-functionalized ionic liquid moieties are covalently bonded to the clay producing an organoclay composite (Figure 1b).

According to %C of **1** in CHN analysis, there are 26 mmol organic residues per 1 g of the organoclay composite. Based on %N of **2**, which originates from imidazolium group, we concluded that 4 mmol of epoxy group has reacted with 1-methyl immidazole to give CCPIL **2**.
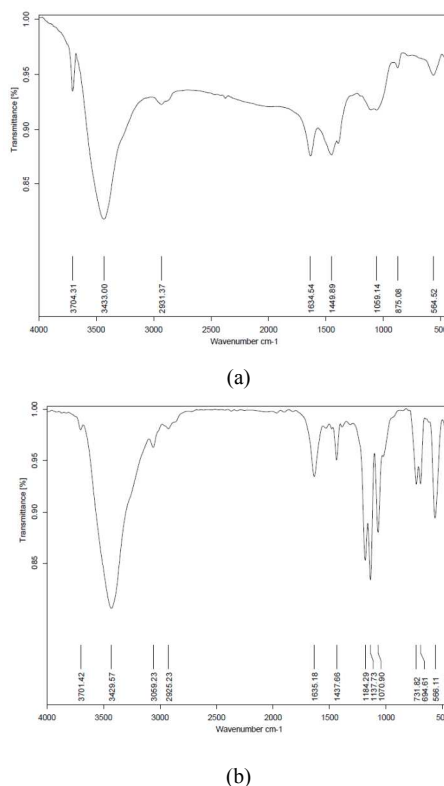

(a)

(b)

Figure 1. FT-IR spectra of (a) epoxy clay **1** and (b) CCPIL **2**

Thermogravimetric analysis (TGA) of **1** confirms the presence of organic groups in the material with decomposition temperature of 200-450 °C affording 62% residual mass (Figure 2a). However, TGA analysis of **2** shows decomposition of organic groups at 200-700 °C giving 39% residual mass (Figure 2b). In comparison with **1**, decreasing the residual mass from 62% to 39% in CCPIL **2**, verifies increasing organic groups which is related to reaction of epoxide moiety with *N*-methyl imidazol and PPh_2Cl.
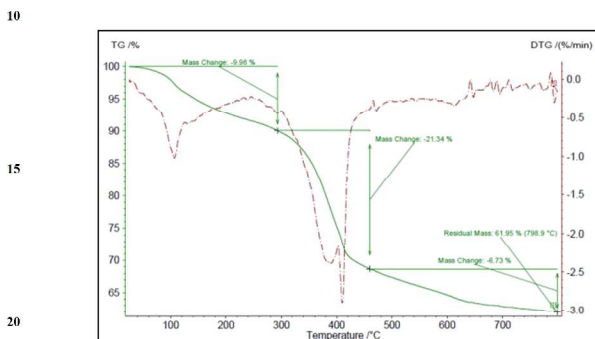
(a)
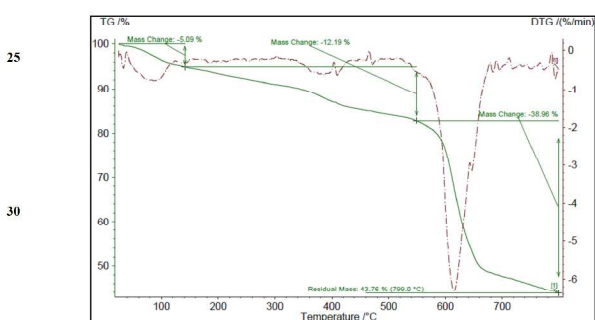
(b)

Figure 2. TGA-DTG of (a) epoxy clay **1** and (b) CCPIL **2**

The complexation of palladium particles with the synthesized organoclay was achieved by stirring the organoclay in an aqueous solution of $PdCl_2$ at room temperature for 24 h. Subsequent washing of filtrate with water in a Soxhlet apparatus (to remove the adsorbed $PdCl_2$) and drying by evacuation at 50 °C for 24 h resulted our target material **3** (Scheme 1). The amount of loading of palladium on the surface of modified clay was determined by ICP analysis to be 0.072 mmol of palladium per 1 g of the composite **3**, showing the high ability of the support to absorb about 72% palladium from the solution. It is very likely that palladium nanoparticles have been mostly ligated by phoshphorus group rather that C-2 position of the immidazole.[16a]

Solid state UV-Vis spectrum of palladium chloride shows a peak at 280 nm corresponding to Pd(II).[18] The reduction of Pd(II) to Pd(0) was confirmed by disappearance of this peak. Moreover, increasing the absorption band in the higher regions indicates the formation of the Pd(0) nanoparticles[19] (Figure 3).

The X-ray diffraction (XRD) pattern of the PdNPs supported on CCPIL shows a low-angle reflection (d_{001}) corresponding to the bilayer arrangement of organic–modified clay.[18] The broad in-plane reflections at higher angles ($d_{020,110}$, $d_{130,200}$) and the

characteristic reflection (060) in smectites confirm the formation of 2 : 1 trioctahedral Mg-organosilicate clay with talc-like structure.[17] The characteristic peaks for Pd(0) can also be observed at (111), (200), (220) and (311) crystallographic planes (Figure 4).[16d]
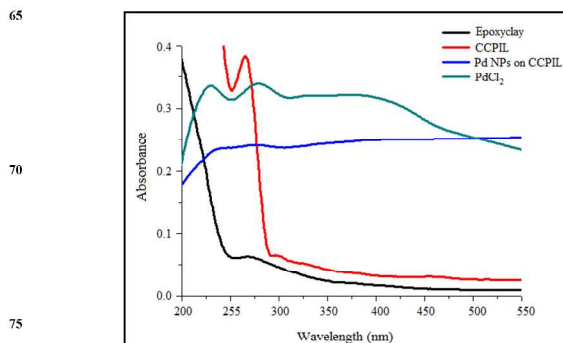

Figure 3. Solid state UV-Vis spectra of $PdCl_2$ (Green line); epoxyclay (Black line); CCPIL (Red line) and PdNPs supported on CCPIL (Blue line)
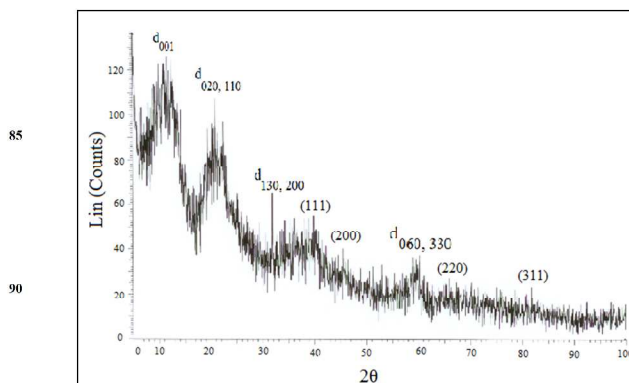

Figure 4. XRD spectrum of palladium nanoparticles supported on CCPIL, **3**

The TEM picture of the supported palladium nanoparticles on the surface of the organoclay composite showed the average size of the palladium particles to be around 3-5 nm, although smaller particles to the size of 1 nm or smaller can also be observed (Figure 5).
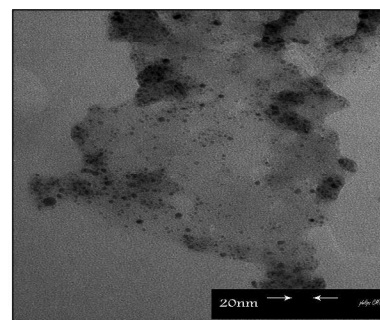

Figure 5. TEM picture of the freshly prepared palladium nanoparticles supported on CCPIL

The morphology of the surface of the composite **3** has been examined by collecting two SEM pictures at two different magnifications (Figure 6). The SEM-EDX pattern indicates the presence of palladium nanoparticles in the structure of the clay
5 composite (Figure 7).

The nitrogen adsorption-desorption isotherm for final catalyst shows type-IV curve with H3 hysteresis loop which is typical for slit-shaped pores (Fig. S1).[20] BET calculations show 84.8 m^2 g^{-1} specific surface area and 0.09 $cm^3 g^{-1}$ total pore volume.
10 After characterization of the composite, it was used as a catalyst for Suzuki-Miyaura reaction. It was found that the use of a combination of an aryl halide (1 mmol), phenylboronic acid (1.2 mmol), palladium nanoparticles deposited on CCPIL (0.01 g containing 7.2×10^{-4} mmol Pd) and NaOH (1.5 mmol), followed
15 by heating in water (3 mL) at 80 °C under air resulted the desired biaryls in excellent yields (Table 1). Since the reactants are insoluble in water, this reaction is an "*on water*" reaction.[21] As shown in Table 1, a range of aryl iodides, bromides and chlorides reacted with phenylboronic acid to give the desired products in
20 high yields. The reaction of iodobenzene (**4a**) was faster in comparison with the aryl iodides bearing an electron donating group (**4b**) or having steric hinderance (**4c**) (Table 1, Entries 1-3). This reaction could be easily conducted at room temperature although in a longer reaction time (Table 1, Entry 1). In the case
25 of 1-iodo-4-aminobenzene (**4b**), the Suzuki-Miyaura reaction was performed exclusively upon carbon halide bond and the *N*-arylation product was not observed (Table 1, Entry 2). The coupling reaction of phenylboronic acid with both electron-releasing and electron withdrawing aryl bromides afforded
30 products in high yields (Table 1, Entry 4-10). Heterocyclic bromides such as 5-bromo pyrimidine (**4h**), 3-bromo thiophene (**4i**) and 3-bromo pyridine (**4j**), led to the corresponding heterobiaryls in high yields (Table 1, Entries 8-10). The catalytic system effect was also manifested for the reaction of aryl
35 chlorides with phenylboronic acid. In these cases, the prolonged reaction times were required to give the expected products in high yields (Table 1, Entries 11-13).
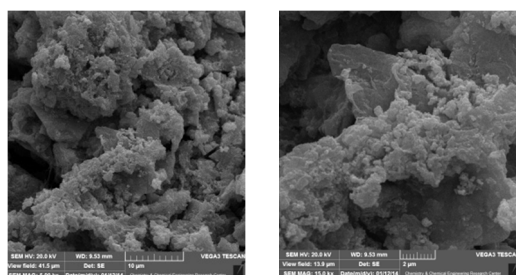

Figure 6. SEM pictures of the composite **3** at two magnifications

50 In comparison with our previously reported system using palladium nanoparticles supported on aminoclay,[16d] the current system is more effective for the activation of C-Cl bonds in the Suzuki-Miyaura reaction. However, this heterogeneous catalyst is much less reactive in Suzuki-Miyaura reaction than the reported
55 water-soluble NHC-Pd polymer with triethylene glycol legs which acts homogeneously.

The reusability of the catalyst was tested upon the reaction of 1-bromo-4-nitro benzene with phenylboronic acid employing

0.01 g of the catalyst in the presence of NaOH at 80 °C. At the
60 first run, the reaction was completed within 2 h to give the product in 90% isolated yield. Similarly, the reactions for the repeated runs were conducted after separation of the catalyst. After completion of the reaction in the first run, the aqueous solution was removed by a syringe. Ethylacetate (5 mL) was
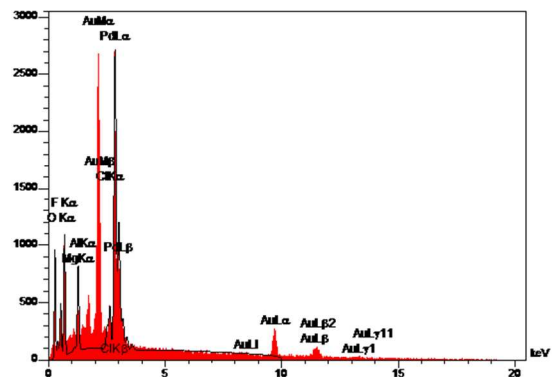65 added to the reaction mixture to extract the organic compounds.

Figure 7. SEM-EDX spectrum of palladium nanoparticles supported on
80 CCPIL

The ethylacetate solution was removed by a syringe and the remained catalyst was dried under nitrogen flow. After complete drying, the catalyst was charged again into the vessel containing
85 the reacting substrates and the reaction was performed under similar conditions. This recycling was repeated for five consecutive runs. As shown in Table 2, no significant changes on the reaction times were observed during the conducted five runs. This observation indicates that, the amounts of leaching of Pd
90 into the reaction mixture should be low. This has been quantitatively approved by ICP analysis, which showed that after five times recycling of the catalyst, only 7% leaching of Pd from the support into the reaction mixture has been occurred.
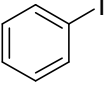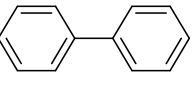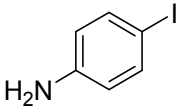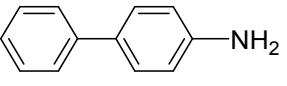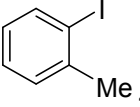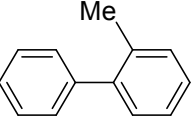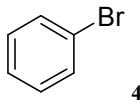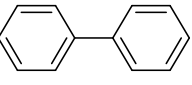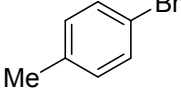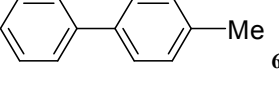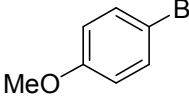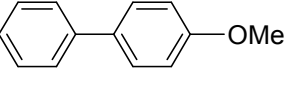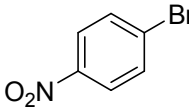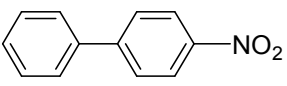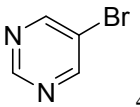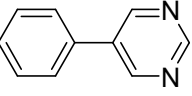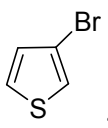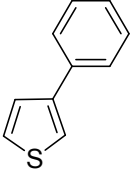
We have also shown that the catalyst is stable towards air. For
95 this aim, we have prepared the catalyst and left it in the air for three months. Then, the catalyst was applied for the reaction of 1-bromo-4-nitrobenzene with phenylboronic acid under the above mentioned conditions. The desired final product was obtained in 88% isolated yield within 2.25 h.
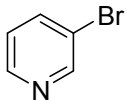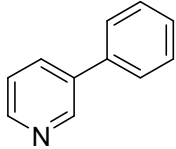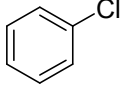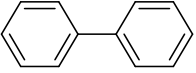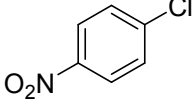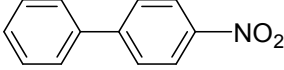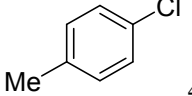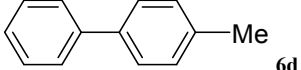100 This composite has also been used for Sonogashira-Hagihara reaction. Inspired by the successful experience from our previous work,[16c] we initiated the optimization study under the conditions reported therein, namely, using KOAc as the base, molten TBAB as the solvent at 100 °C. Employing these conditions, the reaction
105 of 1-bromo-4-nitrobenzene with phenylacetylene went to completion within 40 min (Table 3, Entry 1). Switching the solvent to water gave the desired product in 92% conversion after 6 h (Table 3, Entry 2). Addition of TBAB to the reaction mixture put a good impact on the reaction (Table 3, Entry 3). Different
110 solvents as well as bases were tested for this reaction (Table 3). These studies, like our previous study, led us to choose TBAB as the solvent, KOAc as the base at 100 °C as the optimized conditions.

Utilizing the optimized conditions, a wide range of aryl halides
115 including aryl chlorides reacted with phenylacetylene to give the desired product in high to excellent yields (Table 4). For example

Table 1. Suzuki-Miyaura reaction of various aryl halides with phenylboronic acid in the presence of the catalyst on water
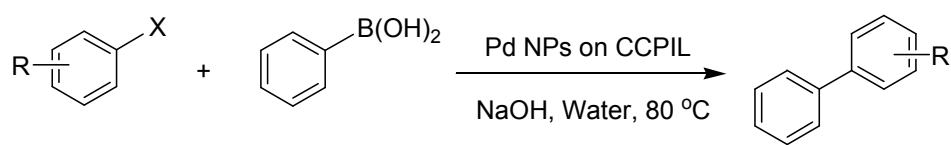

Entry	Substrate	Product	Time (h)	Yield (%)
1	4a	6a	40 min (12)	95 (84)
2	4b	6b	4	91
3	4c	6c	3.5	95
4	4d	6a	9	87
5	4e	6d	10.5	93
6	4f	6e	16	90
7	4g	6f	2	90
8	4h	6g	8	96
9	4i	6h	18	89

10	4j	6i	10	85
11	4k	6a	24	88
12	4l	6f	16	85
13	4m	6d	30	94

Reaction conditions: Aryl halide (1 mmol), phenylboronic acid (1.2 mmol), Pd nanoparticles supported on CCPIL (0.01 g), NaOH (1.5 mmol) on water (3 mL) at 80 °C. The data shown in parenthesis refers to the reaction conducted at room temperature

Table 2. Reusability of the catalyst in reaction between 1-bromo-4-nitrobenzene and phenylboronic acid in the presence of NaOH and 0.01 g of the catalyst on water at 80 °C.
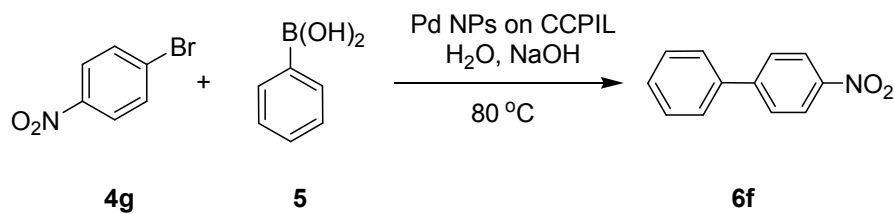
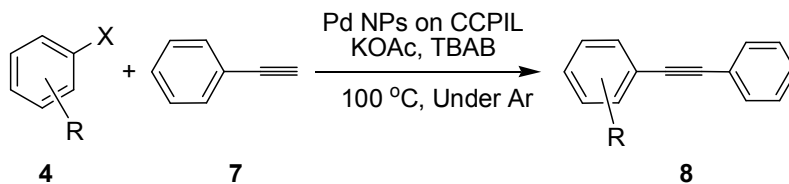| Run	1	2	3	4	5
Time for completion of the reaction (h)	2	2	2	2.25	2.5

Table 3. Optimization conditions in the Sonogashira-Hagihara reaction between 1-bromo-4-nitrobenzene and phenylacetylene in the presence of Pd nanoparticles supported on ionic liquid functionalized clay at 100 °C under argon atmosphere
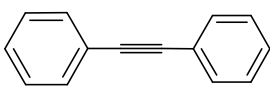

4g   **7**   **8e**
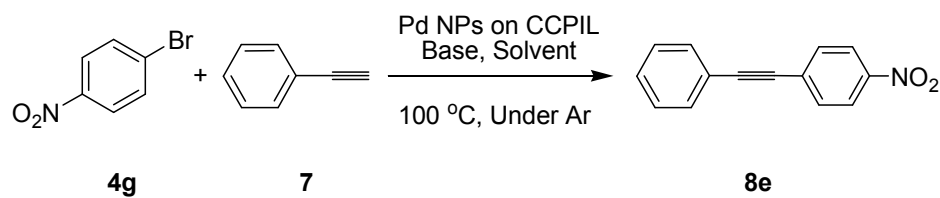
Entry	Solvent	Base	Time (h)	Conversion (%)
1	TBAB	KOAc	40 min	100
2	H_2O	KOAc	6	92
3[a]	H_2O/TBAB	KOAc	2.5	100
4	DMSO	KOAc	3	100
5	PEG400	KOAc	3	100
6	TBAB	NaOAc	1	100
7	TBAB	none	24	23
8	TBAB	Cs_2CO_3	12	100
9	TBAB	NaOH	12	Trace
10	TBAB	Et_3N	12	Trace
11	TBAB	Morpholine	12	Trace

[a] TBAB (1 mmol) was added to the reaction mixture

5

Table 4. Sonogashira-Hagihara reaction of aryl halides with phenylacetylene in the presence of Pd nanoparticles supported on ionic liquid functionalized clay and KOAc in molten TBAB under argon atmosphere

4   **7**   **8**

Entry	Aryl halide	Product	Time (h)	Isolated Yield (%)
1	4a	8a	0.13	96
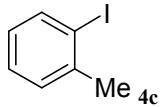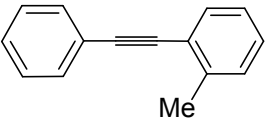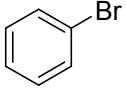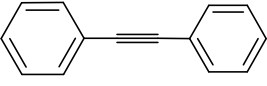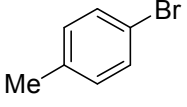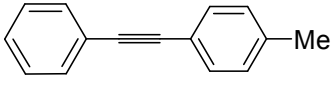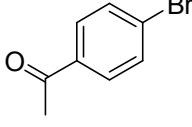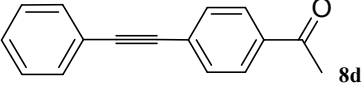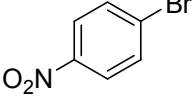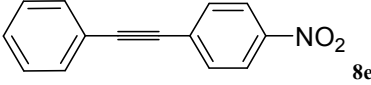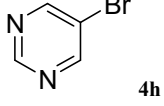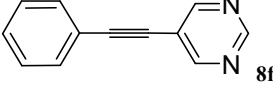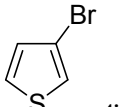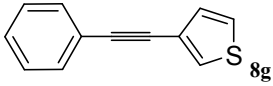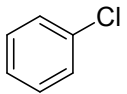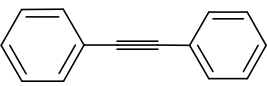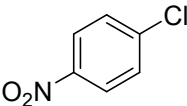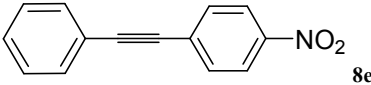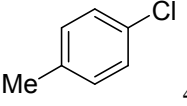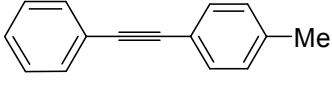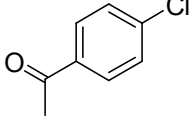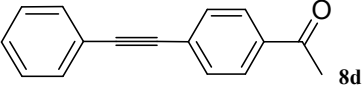
Entry	Substrate	Product	Time	Yield
2	**4c** (2-iodotoluene, I, Me)	**8b**	0.33	91
3	**4d** (Br)	**8a**	1	90
4	**4e** (Br, Me)	**8c**	1	88
5	**4f** (Br, O)	**8d**	2.25	91
6	**4g** (Br, O_2N)	**8e** (NO_2)	0.67	90
7	**4h** (N, Br, N)	**8f**	1	82
8	**4i** (Br, S)	**8g**	1.5	77
9	**4k** (Cl)	**8a**	4	68
10	**4l** (Cl, O_2N)	**8e** (NO_2)	3.5	70
11	**4m** (Cl, Me)	**8c** (Me)	4	76
12	**4n** (Cl, O)	**8d**	3.75	80

Table 5. Reusability of the catalyst in reaction between 1-bromo-4-nitrobenzene and phenylacetylene in the presence of KOAc and 0.01 g of the catalyst in TBAB at 100 °C.

Run	1	2	3	4	5
Time for completion of the reaction (min)	40	40	45	45	45

the reaction of *p*-chloroacetophenone with phenylacetylene gave the desired product in 80% isolated yield within 3.75 h (Table 4, Entry 12). The acetyl group remained intact in this reaction and no condensation reaction was observed.

The catalyst was also recovered for five runs without any significant decrease in its reactivity (Table 5). ICP analysis showed only 3% leaching of the catalyst after the 5th run.

In order to show the wide range of application of the catalyst, we have also applied this nano catalyst in the Mizoroki-Heck reaction. For this purpose, the reaction between bromobenzene and *n*-butyl acrylate using $^{n}Pr_3N$ as the base at 130 °C as the model reaction was studied. As the result presented in Scheme 2, the reaction proceeded smoothly to completion after 12h in the absence of solvent at 130°C to give the desired product in 77% isolated yield.

Scheme 2. Mizoroki-Heck reaction of bromobenzene with *n*-butyl acrylate in the presence of Pd(0) nanoparticles under neat conditions

Conclusions

In conclusion, we have designed and synthesized a new class of supported- ionic liquid on the surface of organofunctionalized clay. To this support, a phosphinite g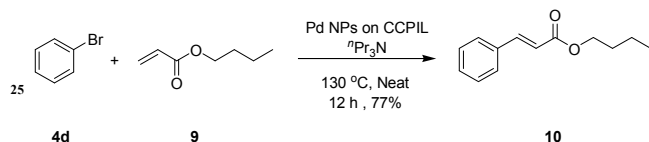roup was anchored to act as a suitable ligand for transition metals. Palladium nanoparticles were deposited on the surface of this support. This composite has been applied as a recyclable catalyst for Suzuki-Miyaura reaction of aryl halides (I, Br and Cl) with phenylboronic acid on water under air atmosphere with small amounts of Pd leaching. The composite is stable towards air and moisture. In order to show the merit of the compound as a catalyst, we have performed Sonogashira-Hagihara reaction in molten TBAB and also Mizoroki-Heck reaction under solvent-free conditions.

Notes and references

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