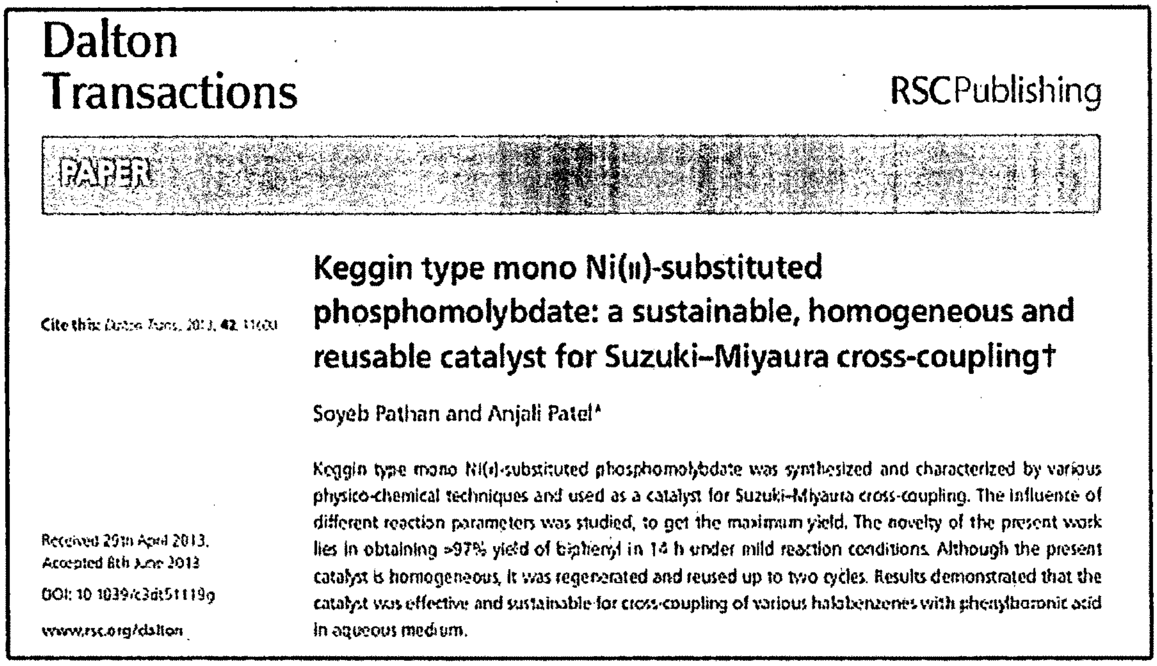
Chapter

7

Use of $PMo_{11}Ni$ as a sustainable catalyst for Suzuki coupling



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Keggin type mono Ni(II)-substituted phosphomolybdate: a sustainable, homogeneous and reusable catalyst for Suzuki–Miyaura cross-coupling†

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Keggin type mono Ni(II)-substituted phosphomolybdate was synthesized and characterized by various physico-chemical techniques and used as a catalyst for Suzuki–Miyaura cross-coupling. The influence of different reaction parameters was studied, to get the maximum yield. The novelty of the present work lies in obtaining >97% yield of biphenyl in 14 h under mild reaction conditions. Although the present catalyst is homogeneous, it was regenerated and reused up to two cycles. Results demonstrated that the catalyst was effective and sustainable for cross-coupling of various halobenzenes with phenylboronic acid in aqueous medium.

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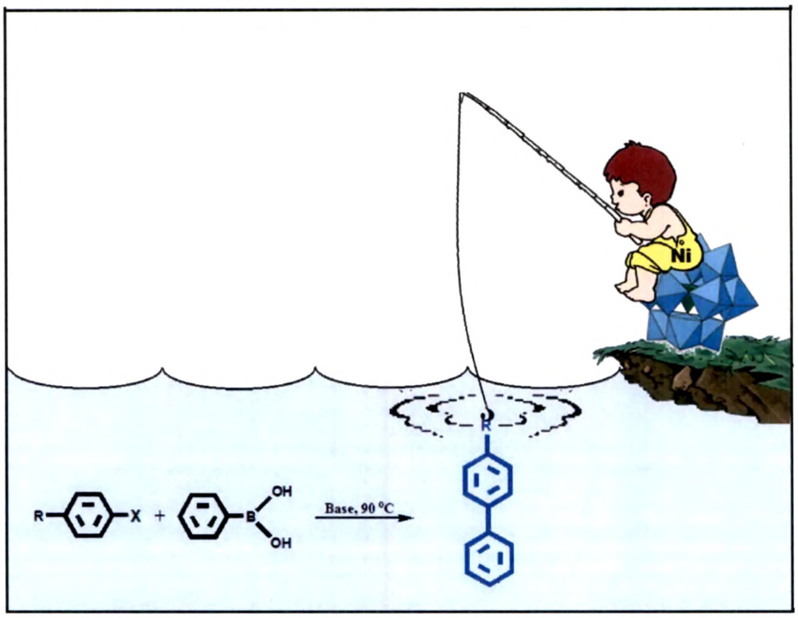


Abstract

Keggin type mono Ni(II)-substituted phosphomolybdate was synthesized and characterized by various physico-chemical techniques and used as a catalyst for Suzuki–Miyaura cross-coupling. The influence of different reaction parameters was studied, to get the maximum yield. The novelty of the present work lies in obtaining >97% yield of biphenyl in 14 h under mild reaction conditions. Although the present catalyst is homogeneous, it was regenerated and reused up to two cycles. Results demonstrated that the catalyst was effective and sustainable for cross-coupling of various halobenzenes with phenylboronic acid in aqueous medium.

Introduction

Suzuki-Miyaura(SM) coupling, generally coupling of aryl halides with organoborons, is an important organic transformation for the construction of C-C bonds and plays a vital role in the synthesis of natural products, pharmaceuticals, and advanced materials.[1] Regarding functional group tolerance and advantages of organoborons compounds as coupling partners, the SM coupling are gaining increasing attention over other optional approaches for C-C bond formation such as Negishi coupling,[2] Kumuda coupling,[3] Kharash coupling,[4] Stille coupling,[5] and Hiyama coupling[6].

Generally, procedure of SM coupling involves the use of precious metal as a catalyst, especially palladium, with ligands such as phosphines,[7] N-heterocyclic carbenes,[8] amines,[9] oximes,[10] and imines.[11] Many of these ligands suffer from the problems such as air/moisture sensitivity, toxicity, cost and commercially unavailability. Although complexes containing such ligands often show excellent activities in organic solvents, incompatibility of most of the ligands with water restricts their use in water. At the same time, reports on Pd-catalyzed SM coupling in neat water are also available.[12] Water has clear advantages over organic solvents in organic synthesis.[13] From environmental point of view, efforts have been focussed towards development of SM coupling catalyzed by ligand free catalysts in aqueous media.

However, reactions in aqueous medium suffer from several difficulties such as low solubility of substrates, slow and/or incomplete conversions and deactivation of metal catalysts owing to the occupation of coordination sites by water molecules.[14] The mentioned difficulties have been overcome by the use of phase-transfer catalysts,[15] aqueous buffer,[7k] and use of co-solvent. Among these, SM couplings in co-solvent i.e. water: organic systems have devoted much attention in recent years. Many reports on use of organic co-solvent with water are available.[10,16]

A recent review[17] on Nickel-catalyzed cross-couplings states "unless a process is viable with very low levels of Pd, or Pt can be used and recycled, or very high levels of Ni are required, a Ni catalyzed approach would be preferred on a cost basis". Therefore from the perspective of economics, it is enviable to develop Ni based catalysts for SM coupling under aqueous medium. Reports on SM couplings, which employed Ni based catalysts effectively, are available in art.[17,18] However, in most of the catalytic processes, organic solvents are employed as the reaction media.

Recently, a subclass of polyoxometalates (POMs), transition metal substituted polyoxometalates (TMSPOMs), has received increasing attention as catalysts due to their unique properties.[19] Reports on coupling reactions catalysed by Pd-substituted POMs precursor,[20] Pd-exchanged POMs,[21] and Pd-exchanged supported POMs[22] are also available. Neumann et al. reported synthesis of Pd_x-($[PW_{11}O_{39}]^{7-}$) nanoclusters from $K_5[PPd(H_2O)_{11}O_{39}].12H_2O$ and successfully used for SM coupling in ethanol/water as a solvent.[20] To the best of our knowledge, no report on catalytic aspect of Ni-substituted polyoxometalates for coupling reactions is available. So, looking to the importance of SM coupling as well as considering economical and ecological aspects, it was thought of interest to develop sustainable catalytic system for SM coupling based on inexpensive metal Ni and POMs under aqueous medium.

Recently, we have reported synthesis and characterization of cesium salt of Keggin type mono nickel(II)-substituted phosphomolybdate ($CsPMo_{11}Ni$) and its use as an efficient catalyst for oxidation of alcohols.[23] So, as an extension of work, here we explore the use of same as a sustainable catalyst for SM coupling in aqueous media. A catalytic activity for recycled catalyst was also evaluated under optimized conditions.

Results and Discussion

Characterization

Generally synthesis of Keggin type transition metal substituted phosphomolybdates has been carried out in two steps (Scheme S1). (i) Synthesis and isolation of lacunary precursor, $PMo_{11}O_{39}^{7-}$ from either parent 12-molybdophosphoric acid (PMo_{12}) or individual transition metal salts (ii) synthesis of transition metal substituted phosphomolybdate by incorporation of transition metal ions into $PMo_{11}O_{39}^{7-}$. In the present work, one-pot synthesis is proposed (Scheme S2). It consists of in-situ formation of $PMo_{11}O_{39}^{7-}$ by addition of NaOH (pH 4.3) to commercially available PMo_{12}. The formed $PMo_{11}O_{39}^{7-}$ was further react with nickel salt (in-situ) to from Ni(II)- substituted phosphomolybdate in good yield (62% yield based on Mo).

The elemental analysis result shows that, found values are in good agreement with analytical values. Anal Calc % : Cs, 26.03; Mo, 41.34; P, 1.21; Ni, 2.30; O, 28.84. Found % : Cs, 26.12; Mo, 41.39; P, 1.24; Ni, 2.32; O, 28.89.

It is observed from Thermo Gravimetric Analysis (TGA) that, catalyst showed initial weight loss of 4.33% upto 50-150 °C (Fig. S1). This may be due to the removal of adsorbed water and water of crystallization, correspond to 7 H_2O molecules. Similarly, Differential Thermal Analysis (DTA) shows an endothermic peak at around 130-140 °C, due to loss of water of crystallization. An exothermic peak in the region 425 °C indicates decomposition of Keggin unit.

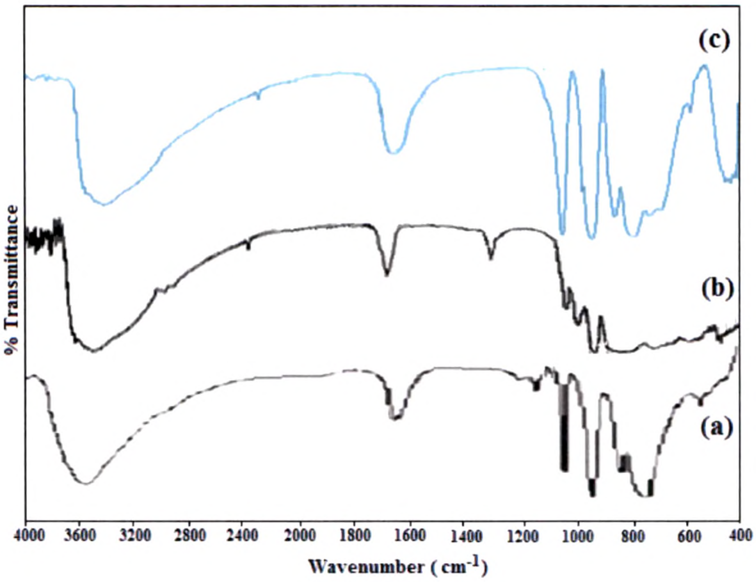


Fig. 1 FT-IR of (a) PMo_{12}, (b) PMo_{11} and (c) $CsPMo_{11}Ni$

The frequencies of Fourier Transform Infrared Spectroscopy (FT-IR) for PMo_{12}, PMo_{11} and $CsPMo_{11}Ni$ are shown in Fig. 1. The FT-IR of PMo_{12} shows bands at 1070 cm^{-1}, 965 cm^{-1} and 870 and 790 cm^{-1} corresponding to the symmetric stretching of P-O, Mo-O_t and Mo–O–Mo bonds respectively. The FT-IR spectra of PMo_{11} shows bands at 1048 and 999 cm^{-1}, 935 and 906 cm^{-1} and 855 cm^{-1} attributed to asymmetric stretches of P-O, Mo-O_t and Mo-O-Mo, respectively. The FT-IR spectra of $CsPMo_{11}Ni$ showed P-O bond frequency 1046 cm^{-1}. The shift in band position as compare to PMo_{12} as well as PMo_{11} indicates that transition metal was introduced into the octahedral lacuna. Shift in the stretching vibration of Mo-O_t and Mo-O-Mo is also observed, indicating the complexation of the transition metals. An additional band 442 cm^{-1} is attributed to Ni-O vibration. Thus, the FT-IR spectra clearly show the incorporation of Ni into the Keggin framework.

The powder X-ray diffraction (XRD) pattern of PMo_{12}, PMo_{11}, and $CsPMo_{11}Ni$ are shown in Fig. 2. PMo_{12} shows characteristic peaks between 10 to 30 2theta, indicating presence of parent Keggin ion. It is also observed that, XRD pattern of $CsPMo_{11}Ni$ is entirely different as compare to PMo_{12}, but similar to PMo_{11}.

This confirms that the synthesized material contains PMo_{11} unit. Slight shifting in 2theta peak value as compare to that of PMo_{11} may be due to the incorporation of Ni into PMo_{11}.

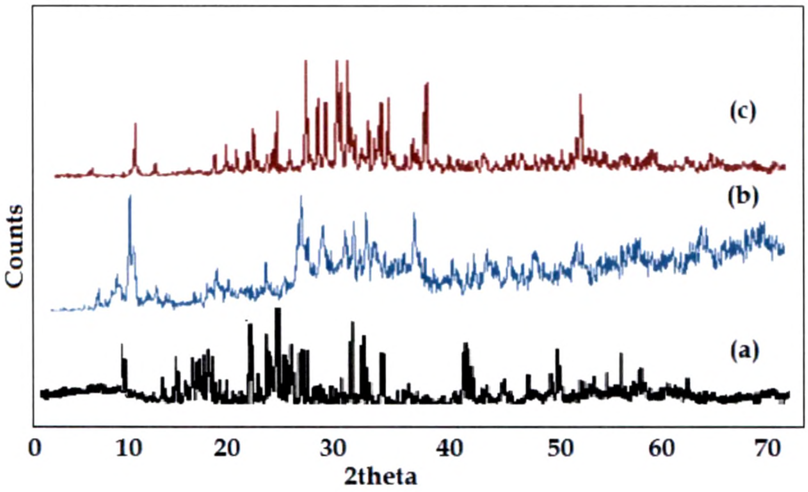


Fig. 2 XRD pattern of (a) PMo_{12}, (b) PMo_{11} and (c) $CsPMo_{11}Ni$

Moreover, XRD pattern of $CsPMo_{11}Ni$ shows crystalline nature of the synthesized material, which is also confirmed by scanning electron microscopy (SEM).

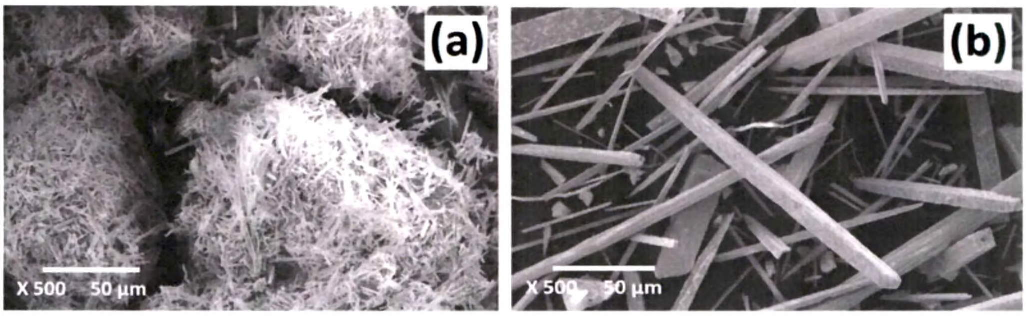


Fig. 3 SEM (a) PMo_{11} and (b) $CsPMo_{11}Ni$ at a magnification 500 X

Fig. 3 (a) shows semi-crystalline nature of PMo_{11}. On incorporation of Ni into lacuna of PMo_{11}, morphology of the material is changed i.e. semi-crystalline character of material transformed to pure crystalline (Fig. 3 b), due to incorporation of Ni into the Keggin framework.

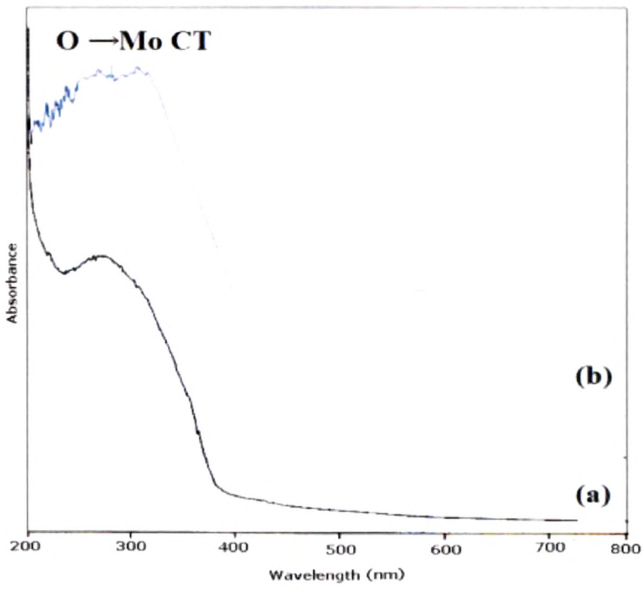


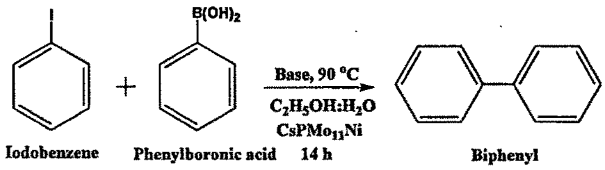
Fig. 4 DRS of (a) PMo_{11} and (b) $CsPMo_{11}Ni$

The Diffused reflectance spectra (DRS) give information about the non-reduced heteropolyanions due to charge transfer from oxygen to metal. DR spectra of PMo_{11} exhibits absorption at 290 nm (λ_{max}) which is attributed to O→Mo charge transfer (Fig. 4). Similar O→Mo charge transfer band at 300 nm was observed for $CsPMo_{11}Ni$. In addition, a broad peak at 550-600 nm is obtained in $CsPMo_{11}Ni$ which arises due to the d–d transitions typical for octahedral transition metal i.e Ni(II), with six oxygen bond ligands.

Catalytic studies

A detailed study was carried out on the SM coupling to optimize the conditions. Initially, effect of bases on coupling of iodobenzene and phenylboronic acid in the presence of $CsPMo_{11}Ni$ in ethanol:H_2O (3:7 mL) was examined at 90 °C (Table 1). The use of inorganic bases, such as Na_2CO_3 and K_2CO_3 gave the cross coupling product in high yield. It is also seen from the Table 1 that poor yield of cross coupling product was obtained when NaOH was used. Organic base such as, Et_3N also show relatively good yield (92%) for present coupling reaction. Among these, K_2CO_3 was selected as base for further studies.

Table 1 Effect of different base

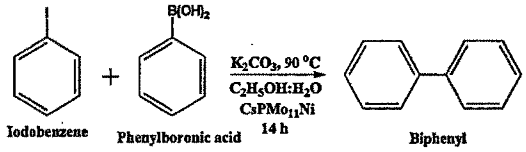


Base	% Isolated Yield[a]
K_2CO_3	97
Na_2CO_3	90
NaOH	77
Et_3N	92

[a] Iodobenzene (1.96 mmol), phenylboronic acid (2.49 mmol), base (3.92 mmol), $C_2H_5OH:H_2O$ (3:7 mL), 0.1mol% catalyst

The effect of concentration of the catalyst on the conversion is shown in Table 2. It is seen from the Table 2 that, with an increase in the amount of catalyst i.e. Ni content, the % yield also increases. This suggests that Ni functions as active site for the coupling reaction. It is observed that that very low concentration of Ni, i.e. 0.1 mol% Ni (1.96 X 10^{-5} mole) is sufficient to obtain excellent yield of biphenyl (97%).

Table 2 Effect of amount of catalyst



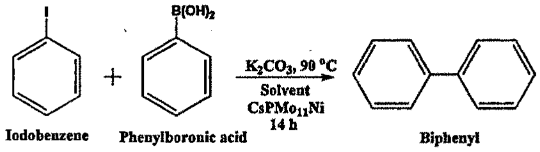
Amount of Catalyst (mg)	Ni Content		% Isolated Yield[a]
	Mole X 10^{-5}	mol %Ni	
30	1.19	0.06	74
40	1.53	0.08	82
50	1.96	0.10	97
60	2.38	0.12	98
100	3.91	0.20	98

[a] Iodobenzene (1.96 mmol), phenylboronic acid (2.49 mmol), K_2CO_3 (3.92 mmol), C_2H_5OH:H_2O (3:7 mL)

Effect of different volume ratio of C_2H_5OH:H_2O was studied and results are summarized in the Table 3 that. Moderate reaction yield (46%) was observed in neat water without any additive. The addition of ethanol as a co-solvent to the reaction mixture greatly accelerated the reaction and increased the yields of biphenyl. The complete conversion and 97% isolated yield was obtained when the reaction was carried out with 3:7 ethanol: water ratio.

Further, to see the effect of other solvents, SM coupling of iodobenzene with phenylboronic acid was carried out in different co-solvents such as methanol, acetonitrile, toluene and dioxane (Table 3, Entry 3). Poor yield of biphenyl was obtained when toluene and acetonitrile use as co-solvent with waters. Almost similar yield of biphenyl was obtained for methanol, ethanol and dioxane. But, considering environmental aspect, relatively green solvent, ethanol was used as a co-solvent for further studies.

Table 3 Effect of volume ratio and effect of different co-solvent

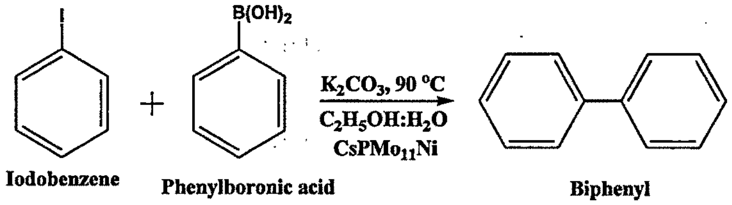


Entry	Solvent ratio (Ethanol: H_2O) mL	% Isolated Yield[a]
1	0: 10	46
2	2: 8	65
3	3:7	97 96[b] 82[c] 33[d] 98[e]
4	5:5	96
5	6:4	93
6	8:2	79
7	10:0	77

[a]Iodobenzene (1.96 mmol), phenylboronic acid (2.49 mmol), K_2CO_3 (3.92 mmol), 0.1mol% catalyst; [b]CH_3OH, [c]CH_3CN, [d]Toluene, [e]Dioxane

The effect of reaction time on the % yield is shown in Table 4. It is seen from Table 4 that with an increase in the reaction time, the % yield also increases. 97% yield was observed at 14 h.

Table 4 Effect of reaction time on the % yield



Time (h)	% Isolated Yield[a]
4	31
8	59
12	84
14	97
16	98

[a] Iodobenzene (1.96 mmol), phenylboronic acid (2.49 mmol), K_2CO_3 (3.92 mmol), 0.1 mol% catalyst, $C_2H_5OH:H_2O$ (3:7 mL)

The optimized condition for the maximum yield of biphenyl was; iodobenzene (1.96 mmol); phenylboronic acid (2.49 mmol); K_2CO_3 (3.92 mmol); 0.1 mol% catalyst (50 mg $CsPMo_{11}Ni$); 10 mL Solvent (3 mL ethanol: 7 mL H_2O); Temperature (90 °C); Reaction time (14 h). The calculated TON for the same is 100.

Control experiments with PMo_{12}, PMo_{11}, Ni-acetate and $CsPMo_{11}Ni$ was also carried out under optimized conditions. It is seen from Table 5 that PMo_{12} and PMo_{11}, are inactive towards the coupling, indicating the catalytic activity is due to only Ni. The same reaction was carried out by taking an active amount of Ni-acetate. Only 40% yield of biphenyl was found for Ni-acetate catalyzed reaction. But at the same, when $CsPMo_{11}Ni$ was used as a catalyst, yield increased drastically.

Table 5 Control experiments

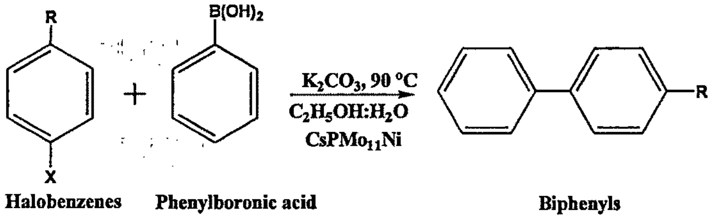
Material	% Yield[a]
PMo_{12}	NC
PMo_{11}	NC
Ni-acetate	40
$CsPMo_{11}Ni$	97

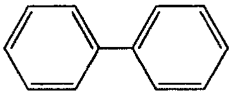
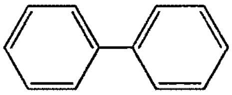
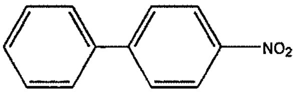
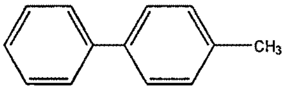
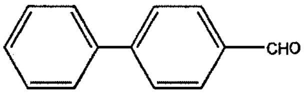
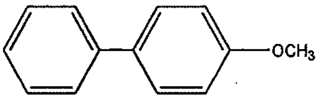
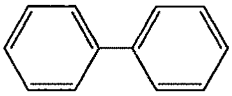
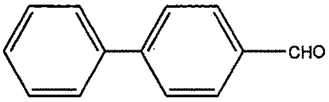
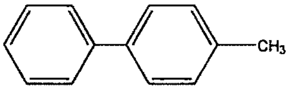
[a]Iodobenzene (1.96 mmol), phenylboronic acid (2.49 mmol), K_2CO_3 (3.92 mmol), 0.1 mol% catalyst, Temperature (90 °C), Reaction time(14 h), NC(no conversion), C_2H_5OH:H_2O (3:7 mL)

From these results, it is understandable that phosphomolybdate plays an important role in coupling. Nevertheless, the role of phosphomolybdate as well as associated mechanism for present coupling reaction is unclear and out of the scope in the present study.

In order to see scope and limitations of substrates in the present catalytic system, SM coupling was also carried out with different halobenzenes and phenylboronic acid under optimized condition (Table 6). The yield obtained by coupling bromobenzene and chlorobenzene with phenylboronic acid was lower as compare to the coupling of iodobenzene with phenylboronic acid i.e. the coupling of iodobenzene with phenylboronic acid is much easier as compared to the coupling of bromobenzene and chlorobenzene, which as expected. So, order of reactivity of different halobenzene is Ph-I > Ph-Br >> Ph-Cl. It is also seen from the Table 6 that substitution on halobenzenes has mark effect on coupling reaction. Substituted bromobenzenes (with electron donating groups (EDGs) such as $-CH_3$, $-OCH_3$), shows low conversion as compare to bromobenzene and required more time for completion of reaction.

Table 6 Coupling of different halobenzenes with phenylboronic acid

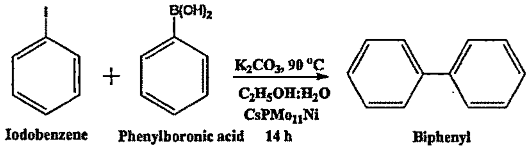


R	X	Product	Time (h)	% Isolated Yield[a]
H	I		14	97
H	Br		14 16	92 98
NO_2	Br		14	98
CH_3	Br		14 20	73 97
CHO	Br		14	96
OCH_3	Br		14 17	78 98
H	Cl		14	15
CHO	Cl		14	23
CH_3	Cl		14	<5

[a]Halobenzene (1.96 mmol), phenylboronic acid (2.49 mmol), K_2CO_3 (3.92 mmol), 0.1 mol% catalyst, $C_2H_5OH:H_2O$ (3:7 mL)

At the same time, substituted bromobenzenes (with electron withdrawing groups (EWGs) such as $-NO_2$, -CHO) has positive effect on coupling and reached to completion with a lesser amount of time as compare to bromobenzene. So, for present catalytic system, order of reactivity of bromobenzenes is, EWGs- Ph-Br > Ph-Br > EDGs- Ph-Br. For chlorobenzenes, the present catalyst shows very poor activity especially for Ph-Cl and EDGs-Ph-Cl. However, In case of EWGs-Ph-Cl, 23% yield of corresponding biphenyl is observed.

Table 7 Recycling of the catalyst



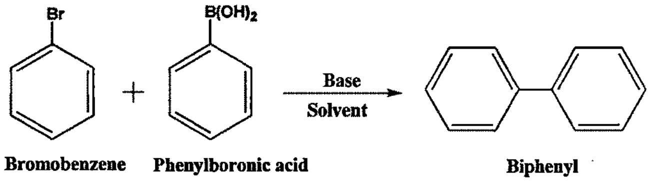
Catalyst	Cycle	% Yield[a]
$CsPMo_{11}Ni$	Fresh	97
	1	92
	2	90
	3	54

[a] Iodobenzene (1.96 mmol), phenylboronic acid (2.49 mmol), K_2CO_3 (3.92 mmol), 0.1 mol% catalyst, $C_2H_5OH:H_2O$ (3:7 mL)

Recyclability of the present catalyst was also explored for coupling of iodobenzene and phenylboronic acid (Table 7) under optimized condition. After completion of reaction, reaction mixture was cooled to room temperature, the organic products were extracted by ethyl ether and the yields were determined. The aqueous phase was then transferred to a new reaction flask for the next cycle. It is seen from the Table 7 that on recycling (cycle 1 and 2), no significant decrease in yield was observed. For third cycle, remarkable change in yield of biphenyl is observed. This may be due to decomposition of Keggin framework into their corresponding metal oxides. So, the present catalysts can be reused upto two cycles only.

Table 8 represents comparison of catalytic activity of present catalyst with reported catalysts. Cho et al. reported coupling of bromobenzene with phenylboronic acid in the presence of nickel(0) powder along with addition of I_2 in PEG-400 at 110 °C to afford biphenyl in high yield.[24] On comparison with present reaction system, the reported reaction was carried out at relatively high temperature (110 °C). Moreover, to increase the rate of reaction, I_2 has been added. So, the present system is better as the reactions were carried out under mild conditions without addition of I_2.

Table 8 Comparison of catalytic activity with reported catalyst



Catalyst	Reaction conditions*	T (°C)	% Yield	Ref.
[a]Ni(0)-powder	1:1.2:2:2:10	110	95	24
[b]Pd_x-([$PW_{11}O_{39}$]$^{7-}$	1:2:2.5:10:12	80-85	94	20
[c]$CsPMo_{11}Ni$	1.96:2.49:3.92:10:14	90	97	Present Work

*PhBr (mmol): $PhB(OH)_2$ (mmol): Base (mmol): solvent (mL): Time(h);

Base: K_2CO_3[a,c]/ diisopropylamine[b]

Solvent: PEG-400 (2mL)[a], C_2H_5OH:H_2O (3:7 mL)[c]/ C_2H_5OH:H_2O (2:8 mL)[b]

Pd_x-($[PW_{11}O_{39}]^{7-}$) catalyzed cross coupling of bromobenzene(1 mmol) with phenylboronic acid in 10 mL EtOH:H_2O at 80-85 °C has been reported by Neumann et al.[20] On comparison with present catalyst it was found that, almost similar yield of biphenyl was obtained. But, form economical point of view, the present catalyst is superior as Ni was replaced with precious metal Pd.

Conclusions

In conclusion, we have come up with sustainable catalytic system for Suzuki–Miyaura cross-coupling reactions catalyzed by Ni(II)-substituted phosphomolybdates under mild reaction conditions. With very low loading of catalyst (0.1 mol% Ni), good-to-excellent yields (73-98%) of the coupling products were obtained under aqueous medium. The present catalytic system has good functional group tolerance and to be broadly applicable to a variety of halobenzenes (X = I, Br) and also some extend to chlorobenzenes bearing electron withdrawing group. The catalysts can be re-used up to 2 cycles with slight decrease in yield of biphenyl. The advantages of using a recyclable Ni instead of more expensive metals, and using aqueous medium makes this methodology interesting from a economical and ecological point of view.

Experimental Section

Materials

All chemicals used were of A. R. grade. $H_3PMo_{12}O_{40}$, sodium hydroxide, phenylboronic acid, iodobenzene, bromobenzene, chlorobenzene, 1-bromo-4-nitrobenzene, 4-bromotoluene, 4-bromobenzaldehyde, 4-bromoanisol, 4-chlorotoluene, 4-chlorobenzaldehyde, petroleum ether, ethyl acetate, $Ni(CH_3COO)_2.4H_2O$ were obtained from Merck and used as received.

Synthesis of Nickel substituted phosphomolybdates ($CsPMo_{11}Ni$)

$H_3PMo_{12}O_{40}$ (PMo_{12}, 1.825 g, 1mmole) was dissolved in of water (10mL) and the pH of the solution was adjusted to 4.3 using sodium hydroxide solution.

$Ni(CH_3COO)_2$. $4H_2O$ (1mmole) dissolved in minimum amount of water was mixed with above hot solution. pH of solution was adjusted to 4.3. The solution was heated at 80° C with stirring for 1 h and filtered hot. To the hot filtrate saturated solution of CsCl was added drop wise and allowed to stand. The obtained tiny crystals (62 % yield) were filtered, air dried and designated as $CsPMo_{11}Ni$.

Characterization

The synthesized materials were characterized by elemental analysis, TG-DTA, FT-IR, powder XRD and DRS. Elemental analysis was carried out using the JSM 5610 LV EDX-SEM analyzer. TG-DTA was carried out on the Mettler Toledo Star SW 7.01 up to 600°C in air with the heating rate of 5°C/min. FT-IR spectra of the samples were recorded as the KBr pellet on the Perkin Elmer instrument. The powder XRD pattern was obtained by using the instrument Philips Diffractometer (Model PW- 1830). The conditions used were Cu Kα radiation (1.5417A°).The UV-Visible-DR spectrum was recorded at ambient temperature on Perkin Elmer 35 LAMDA instrument using the 1 cm quartz cell.

Catalytic reaction

The SM coupling was carried out in a in a glass batch reactor (50 mL) with a magnetic stirrer. H_2O was degassed with N_2 before use. In the experiment, halobenzene (1.96 mmol), phenylboronic acid (2.94 mmol), base (3.92 mmol) and C_2H_5OH: H_2O (10 mL) containing 0.1 mol% catalyst (50.0 mg $CsPMo_{11}Ni$) were added into the reactor. Then the reactor was heated to the desired temperature in an oil bath with stirring under N_2 atmosphere. After reaction, product was collected by extraction of diethyl ether. The organic phases were then dried with anhydrous magnesium sulphate, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with a mixture of ethyl acetate and petroleum ether as eluent. Isolated Product was identified by ^1H NMR. In all reaction traces of homo coupling product was found.

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