J. Chem. Sci. (2021)133:8
https://doi.org/10.1007/s12039-020-01870-6

REGULAR ARTICLE

Bimetallic nano alloy architecture on a special polymer: Ni or Cu merged with Pd for the promotion of the Mizoroki–Heck reaction and the Suzuki–Miyaura coupling

VIJAY P PATIL[a,b], ABHIJIT A KASHID[a], BHANUPRATAP S SOLANKI[b,d], ULHAS K KHARUL[c,d] and SURESH IYER[a,d,*]
[a]Organic Chemistry Division, National Chemical Laboratory, Dr. Homi Bhabha Road, Pashan, Pune 411008, Maharashtra, India
[b]Chemical Engineering and Process Development, National Chemical Laboratory, Pashan, Pune 411008, Maharashtra, India
[c]Polymer Science and Engineering Division, National Chemical Laboratory, Dr. Homi Bhabha Road, Pashan, Pune 411008, Maharashtra, India
[d]Academy of Scientific and Innovative Research (AcSIR), New Delhi 110025, India
E-mail: s.iyer@ncl.res.in

MS received 28 August 2020; revised 23 October 2020; accepted 29 October 2020

Abstract. Novel Ni-Pd and Cu-Pd bimetallic nano alloys was designed and heterogenized on the highly robust ABPBI [poly(2,5-benzimidazole)] polymer in high yields using $NaBH_4$ as reducing agent. These were versatile ligand free catalysts for the Mizoroki–Heck reaction and Suzuki–Miyaura coupling. The bimetallic Ni-Pd-ABPBI catalyst for the Mizoroki–Heck reaction of 4-iodo anisole could be recycled 5 times with high yields. Aryl bromides could also be activated for the Mizoroki–Heck reaction using Cu-Pd-ABPBI NP catalysts, with moderate yields.

Keywords. Bimetallic nano alloys; Mizoroki–Heck reaction; Suzuki coupling; Ni-Pd-ABPBI; Cu-Pd-ABPBI.

1. Introduction

Nanoparticles are state-of-the-art for catalysis while bimetallic nano alloys exhibit greater enhancement in efficiency due to the harmonic interaction of a noble metal with a lighter metal, thus becoming a successful & flourishing strategy for noble metal catalysis. Heterogenization of noble metal catalysts on insoluble supports like SiO_2, Al_2O_3, is a common and successful solution being experimented. Recovery of noble metal and efficient use in smaller quantities makes this an industrially viable alternative and next generation catalysis.

C-C bond forming reactions plays a pivotal role in mimicking the nature in the laboratories and to develop molecular scaffolds and organic compounds possessing complex molecular architecture. The practical solution lies in the development of inexpensive transition metals and/or recovery and recyclability of the catalytic system with improved selectivity and catalytic efficiency. Bimetallic catalysts are known to be superior to the corresponding mono metallic catalysts for various reactions.[1–7]

The synergistic effect of bimetallic catalysis has been described in the isolated metal atom geometry strategies for catalysis of hydrogenation reaction.[8] In bimetallic catalysis, the exploitation of more expensive noble metal is conserved, with the catalysis being augmented by a less expensive co-catalyst. Inexpensive Ni complexes, Cu salts and heterogeneous catalyst based on Ni, Cu, Co and Mn have activated the Mizoroki–Heck reaction and Suzuki–Miyaura coupling.[9–14]

Ligand free $Pd(OAc)_2$ activates aryl bromides for the Mizoroki–Heck reaction.[15] Bozell and Vogt have

---

*For correspondence

Electronic supplementary material: The online version of this article (https://doi.org/10.1007/s12039-020-01870-6) contains supplementary material, which is available to authorized users.

described the co-operative effect of $NiBr_2$ with $Pd(OAc)_2$ in the presence of excess NaI to activate the relatively unreactive aryl chlorides for the Mizoroki–Heck reaction.[16] The Pd-PMI [poly(imidazole/Palladium)] as a self-assembling supported catalyst has been exemplified for allylation and Suzuki coupling.[17] Heterogenization of bimetallic catalysts on polymer support has the advantages of catalyst recovery and recyclability.[18–23] Ni-Pd bimetallic nano composites catalyze the Suzuki coupling of hindered aryl bromides.[24]

Pd and Pd-Ni bimetallic catalysts supported on multi-walled carbon nano tubes show very high catalytic activity for the Mizoroki–Heck, Suzuki, Hiyama and Sonogashira coupling reactions.[25] The bimetallic catalysis described has the advantage of being ligand free as well as the catalyst can be recycled. ABPBI [poly(2,5-benzimidazole)] is a highly stable polymer with zero solubility in most organic solvents, thus providing a robust heterogeneous support medium comparable to inorganic supports like SiO_2, Al_2O_3, for bimetallic catalysts.[26] Furthermore it has a very high glass transition temperature (T_g) ~ 450 °C, indicating stability at high temperatures.

ABPBI has not been studied as a heterogenous medium for NPs (nano particles), bimetallic NPs or transition metal catalysis. There is only one report on the use of Pd NP on mesoporous-PBI [(poly(2,5-benzimidazole)] for the Suzuki coupling.[27] The activation of atom economical aryl bromides and chlorides is still a challenging task in the Mizoroki–Heck reaction and related cross couplings. Several solutions have been arrived at this activation of aryl bromides using ligands and additives.[28] Bimetallic catalysts have been shown to catalyze the aryl bromide activation in the Sonogashira coupling.[3] The hybrid noble metal merged with non-noble metal nano alloys Pd/Cu, Co, Ni, Fe heterogenized on polymers, graphene or titania demonstrate an enhancement in specific properties due to synergism.[29–32] Based on these observations we designed the bimetallic nano alloys of Cu-Pd and Ni-Pd heterogenized on the functional ABPBI polymer. To conserve the usage of expensive noble metal Pd, the hybrid structure alloyed by Pd and non-noble (Ni, Cu) metals was designed and synthesized. The atom economical aryl bromide activation with this catalysts was also explored.

2. Experimental

2.1 *General procedure for the Ni-Pd-ABPBI catalyzed Mizoroki–Heck reaction of aryl iodides and bromides*

To a solution of Ni-Pd-ABPBI (0.050 g, 0.178 mmol) in 5 ml solvent (PEG-400) was added aryl iodide (1 mmol), alkene (1.5 mmol) and base, Cy_2NMe (1 mmol). The resulting mixture was heated to 150 °C for 2–6 h under argon. After completion, the reaction (monitored by TLC), was quenched by addition of water. The aqueous solution was extracted with ethyl acetate (3 x 20 mL) and the combined organic extract was washed with brine and dried over Na_2SO_4. The organic layer was concentrated *in vacuo* and the crude product purified by column chromatography on silica gel (100–200 mesh, Petroleum ether or Petroleum ether: 2–5% Ethyl acetate) to give the pure product.

2-Propenoic acid-3-phenyl, ethyl ester (2E) (3a) (1.5 h, 0.131 g, 0.75 mmol, 75% yield, colourless oil) CAS Registry Number 103-36-6, ^1H NMR ($CDCl_3$, 200MHz, δ ppm): 7.70 (d, J=16.0 Hz, 1H), 7.47–7.60 (m, 2H), 7.31–7.46 (m, 3H), 6.45 (d, J=16.0 Hz, 1H), 4.28 (q, J=7.1 Hz, 2H), 1.35 (t, J=7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz, δ ppm): 165.95, 144.58, 134.48, 130.22, 128.88, 128.05, 118.30, 60.47, 14.34; HRMS-ESI: $[M^++H]^+$ calcd for $C_{11}H_{12}O_2$ $[M+H]^+$ 177.091, found: 177.091.

2.2 *Procedure for recycle study of catalyst (Ni-Pd-ABPBI)*

To a solution of Ni-Pd-ABPBI (0.050 g, 0.178 mmol) in 5 mL solvent (PEG-400) was added 4-iodo anisole (1 mmol), styrene (1 mmol) and base, Cy_2NMe (1 mmol). The resulting mixture was heated to 150 °C for 2–6 h under argon. After completion, the reaction (monitored by TLC), was filtered to recover the catalyst and the filtrate quenched by addition of water. The aqueous solution was extracted with ethyl acetate (3 x 20 mL) and the combined extract was washed with brine and dried over Na_2SO_4. The organic layer was concentrated *in vacuo* and the crude product purified by column chromatography on silica gel (100–200 mesh, Petroleum ether) to give the pure product. The recovered catalyst was then added to a fresh solution of the reaction mixture and the process repeated for 4 more times (5 cycles).

A4 Benzene, 1-methoxy-4-[(1E)-2-phenylethenyl]-(E) (3d) (1.75 h, 0.191 g, 89%, 0.89 mmol, White solid, M.p. −136 °C) CAS Registry Number 1694-19-5 ^{1}H NMR (CHLOROFORM-d, 200 MHz, δ ppm): 7.31–7.69 (m, 7H), 7.17 (d, J=7.5 Hz, 2H), 7.05 (d, J=8.7 Hz, 2H), 3.97 (s, 3H); ^{13}C NMR (CHLOROFORM-d, 50 MHz, δ ppm): 159.4, 137.7, 130.2, 129.5, 128.7, 128.4, 128.4, 128.3, 128.2, 127.8, 127.7, 127.3, 126.7, 126.3, 114.2, 113.6, 113.0, 77.7, 77.1, 76.5, 55.4; IR (cm^{-1}) 3017, 2925, 2850, 1602, 1510, 1452, 1298, 1253, 1218, 1177, 1113, 1030, 967, 906, 819, 761, 687; HRMS-ESI: $[M^+ + H]^+$ calcd for $C_{15}H_{15}O$, 211.112 found: 211.1114

2.3 *General procedure for Ni-Pd-ABPBI catalyzed Suzuki coupling of aryl iodides*

To a solution of aryl iodide (0.5 mmol), aryl boronic acid (0.6 mmol), TBABr (0.5 mmol) and base, K_3PO_4 (0.6 mmol) in 10 mL solvent Dioxane: Water (1:1) was added Ni-Pd-ABPBI (0.025 g, 0.085 mmol). The resulting mixture was heated to 120 °C for 2–2.5 h under argon. After completion, the reaction (monitored by TLC), was quenched by addition of water. The aqueous solution was extracted with ethyl acetate (3 x 20 mL) and the combined organic extract was washed with brine and dried over Na_2SO_4. The organic layer was concentrated in vacuo and the crude product purified by column chromatography on silica gel (100–200 mesh, Petroleum ether) to give the pure product.

1,1′-Biphenyl (6a) (2 h, 0.067 g, 0.435 mmol, 87% yield, white solid, M.p. −68 °C) CAS Registry Number 92-52-4 ^{1}H NMR (200 MHz, $CDCl_3$, δ ppm) – 7.62–7.56 (m, 4 H), 7.49–7.3 (m, 6 H) IR (cm^{-1}) – 3383, 2965, 2725, 1947, 1879, 1711, 1570, 1457, 1374, 1307, 1163, 1080, 968, 729; HRMS-ESI: $[M]^+$ calcd for $C_{12}H_{10}$ $[M]^+$ 154.078, found: 154.078

3. Results and Discussion

The bimetallic nano alloy catalysts were prepared by the simultaneous reduction of a mixture of copper acetate or nickel acetate, palladium acetate and polymer ABPBI, in ethylene glycol or DMSO as solvent, using $NaBH_4$.[33] Ni-Pd was prepared by the $NaBH_4$ reduction of a mixture of $Pd(OAc)_2$ and $Ni(OAc)_2$ in the presence of ABPBI, in a 1:10:20 ratio. Similarly, Cu-Pd was prepared from a mixture of $Pd(OAc)_2$ and $Cu(OAc)_2$ by reduction with $NaBH_4$ in the presence of ABPBI (1:10:10) (Scheme 1). The catalysts were characterized by XRD, XPS, TEM, FE SEM methods (Figures 1, 2, 3, 4, 5, 6).

The synthesized catalysts were analysed by XRD. Figure 1 represents the XRD of Pd-Cu and Pd-Ni bimetallic catalysts loaded on polymeric PBPBI. It reveals that Pd-Cu/ABPBI show better crystallinity than Pd-Ni/ABPBI. Pd-Cu/ABPBI shows peaks at 2θ=. 42.45° (111) and 74.21° (220) corresponding to the metallic Cu with JCPDS #85-1236 (Supplementary Information).[34]

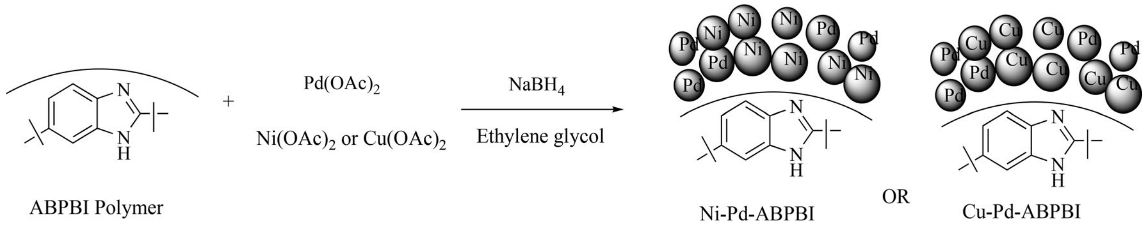
Most intense peak was observed at 2θ= 36.35° which shows that CuO phase is also present in bimetallic composite. Interestingly a different phase of $CuPdO_2$ was observed with 2θ value of 29.86° and 61.37^o. Presence of Oxygen having different environment in XPS confirm this finding which also suggests about the harmonius interaction between both Pd and Cu. Pd was not observed clearly in XRD because of its less concentration in the composition. In case of Pd-Ni/ABPBI there was an instrumental error due to which the peaks have been shifted by the value of −3°. 3 prominent peaks were observed at 2θ value of 26.51° (29.51), 40.36° (43.36°) and 47.05° (50.05°). Lower 2θ value i.e., 29.51° represents Ni_2O (002) whereas the other two can be because of metallic Ni as reported elsewhere. 111 and 200 plane of metallic Ni are represented by 2θ = 43.36° and 50.05° corresponding to JCPDS #70-0989.

Figure 2 represents the SEM-EDX observations of Pd-Ni/ABPBI. The micrograph suggests round morphology of particles distributed in polymeric support at around 500 nm scale. EDX pattern is also in coherence with our calculated value of Pd and Ni. Similar observations were seen in SEM-EDX pattern of Pd-Cu/ABPBI as represented in Figure 3.

Here dispersion of metallic particles was found in form of aggregated clusters which can be the reason of more crystallinity observed in XRD than Pd-Ni/ABPBI. In order to find out the particle size and intensity of dispersion TEM imaging was performed. Figure 4 represents a combined image of both Pd-Ni/ABPBI and Pd-Cu/ABPBI with TEM-EDX.

3.1 *EDX pattern followed by atomic and weight percent of Pd and Ni on ABPBI*

Spherical particle morphology was also confirmed by TEM imaging. Aggregation of clusters was observed in both Pd-Cu/ABPBI and Pd-Ni/ABPBI catalysts. After calculation of 50 nanoparticles the size of Pd-Ni/



Scheme 1. Bimetallic NP Catalyst Preparation & Structure.

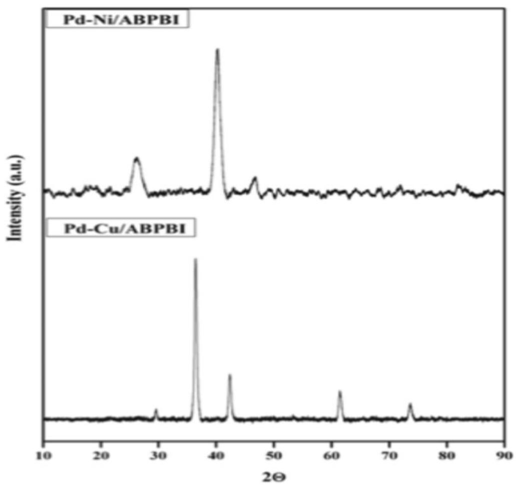
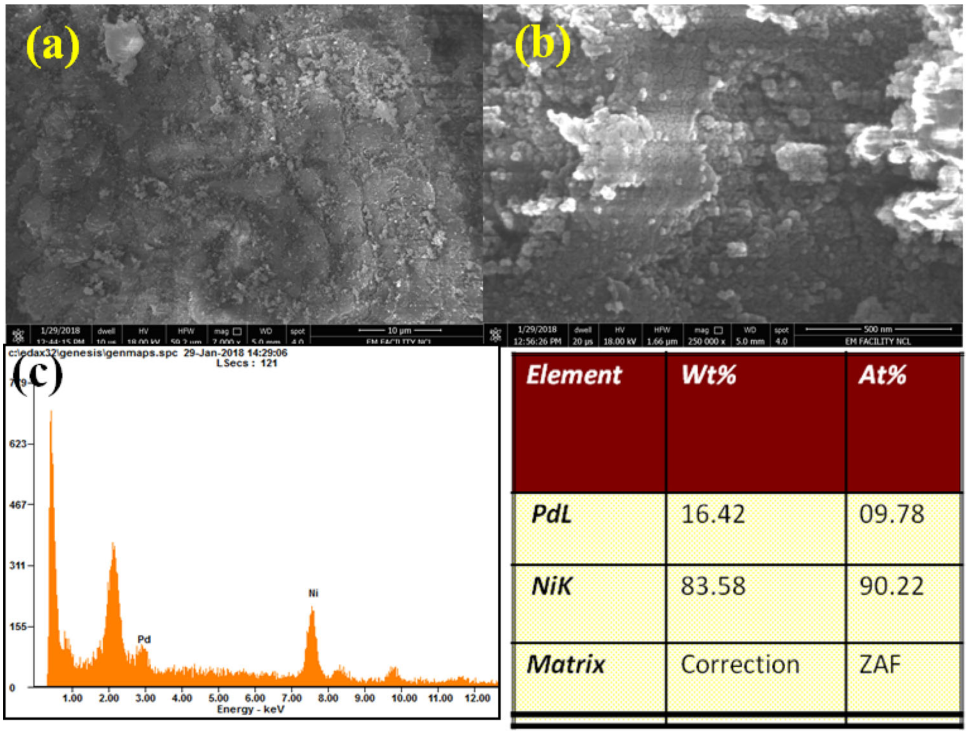


Figure 1. XRD pattern of Pd-Cu and Pd-Ni bimetallic catalysts supported on ABPBI.

ABPBI was observed around 6.68 nm whereas the size of Pd-Cu/ABPBI was 4.47 nm.

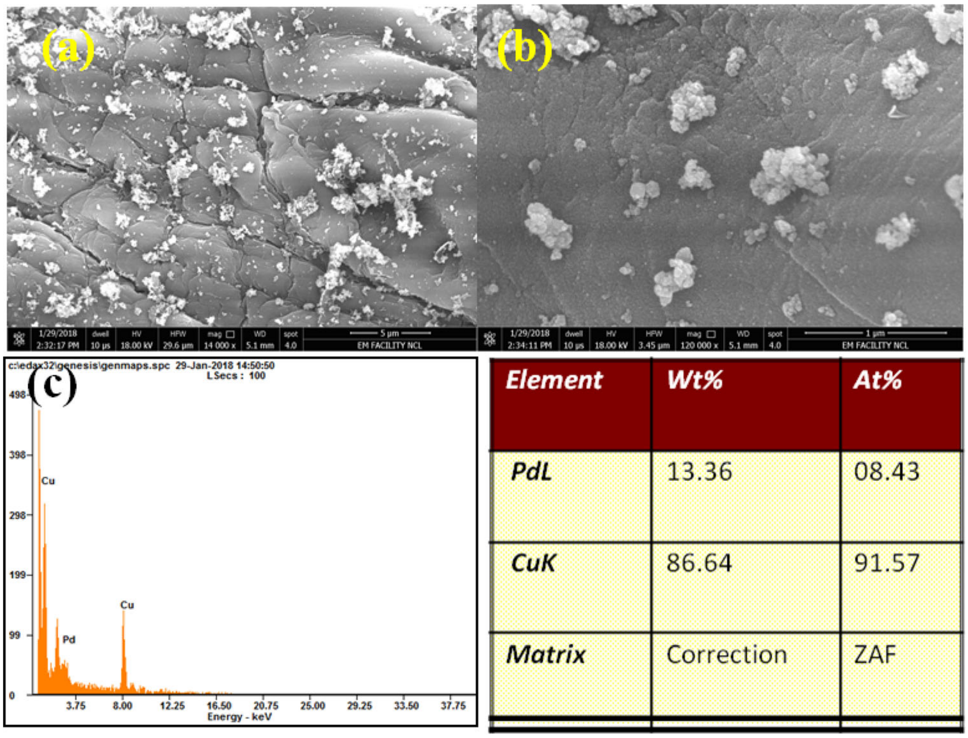
The FE SEM data shows clearly Cu-Pd bimetallic nano clusters adhering to the surface of the polymer support. The aggregated clusters are of non-uniform distribution with sizes of around 500 nm. The Ni-Pd on the other hand are embedded in the polymer support with a micro porous nature. The polymer surface is broken. The FE SEM EDAX shows ratio of Cu:Pd is 6.5:1 while Ni:Pd is 5.1:1. The TEM data shows poly dispersed Cu-Pd bimetallic nano particles with a size distribution of 3.5 nm to 5.8 nm. The Ni-Pd is also poly dispersed with a size distribution ranging from 3.5 nm to 8.9 nm.

Synthesis of metal-metal oxide nanohybrid pairs was concluded by XPS analysis of our screened cat-



Element	*Wt%*	*At%*
PdL	16.42	09.78
NiK	83.58	90.22
Matrix	Correction	ZAF

Figure 2. SEM-EDX of Pd-Ni/ABPBI. (**a**) SEM image at 30 μm (**b**) SEM image at 500 nm (**c**) EDX pattern followed by atomic and weight percent of Pd and Ni on ABPBI.



Element	Wt%	At%
PdL	13.36	08.43
CuK	86.64	91.57
Matrix	Correction	ZAF

Figure 3. SEM-EDX of Pd-Cu/ABPBI. (**a**) SEM image at 5 µm (**b**) SEM image at 1 µm (**c**).

alysts (Figures 5, 6). Both the Pd-Cu/ABPBI and Pd-Ni/ABPBI shows presence of Pd and PdO at their respective binding energy *i.e.* ~335 eV and ~340 eV, respectively. Metallic Cu was observed around 932.33 eV. Presence of strong satellite peaks in Cu deconvolution also revealed the existence of Cu-CuO pair.

These trends continued in the case of Ni also where different types of oxides coexist with metallic Ni with slight shift in BE due to quantum size effect around at 856–864 eV. The nature of Carbon and Oxygen surface was found almost similar in both the cases as the support system was same. Strong proofs of aromatic conjugated carbon bonded with -NH_2 group and framework N-C=O was there with C 1s deconvolution at the B. E. of 285 and 288 eV.

Similarly lattice oxygen, lateral oxygen with different chemical environment and adsorbed oxygen was observed at ~530, 531 and 533 eV, respectively. The presence of metal-metal oxides nano pairs and their complex mutual electron interaction can be one of the reasons for excellent activity of our catalysts.

Various aryl iodides gave high yields for the Mizoroki–Heck reaction, using Ni-Pd-ABPBI as catalyst, with styrene and ethyl acrylate, in short reaction times (Scheme 2) (Table 1). Here, Cy_2NMe was the base of choice while K_2CO_3 and NaOAc gave lower yields. In the reaction with K_2CO_3, the aryl iodides were consumed in short reaction times and the yields were moderate.

Solvent variation was also tried and using PEG-400 gave good results with recoverability of the polymer supported catalyst by simple filtration after the reaction was complete. Recycle studies of the catalyst for the Mizoroki–Heck reaction of 4-iodo anisole with styrene was carried out. The catalyst was active even after 5 recycles giving high yields (62% to 97%) in each cycle (Table 2).

Leaching studies was also carried out with the Ni-Pd-ABPBI catalyst. A blank reaction was carried out without alkene for 6 h at 150 °C. The catalyst was then filtered off and styrene added to the filtrate which was then again heated to 150 °C in an oil bath. Monitoring by TLC showed formation of product. The reaction took a longer 23 h for completion with 63% yield of the Mizoroki–Heck reaction product. This shows some leaching of the catalyst.

The reaction of aryl bromides with Ni-Pd-ABPBI catalyst gave very low yields. So we tried using Cu-Pd-ABPBI as catalyst (Scheme 3). Cu-Pd-ABPBI showed moderate activity for the Mizoroki–Heck reaction of aryl bromides (Table 3). 4-Bromo anisole showed good activity while the other bromides gave only moderate reactivity. A high yield of 87% was obtained in the reaction of 2-bromo benzaldehyde with

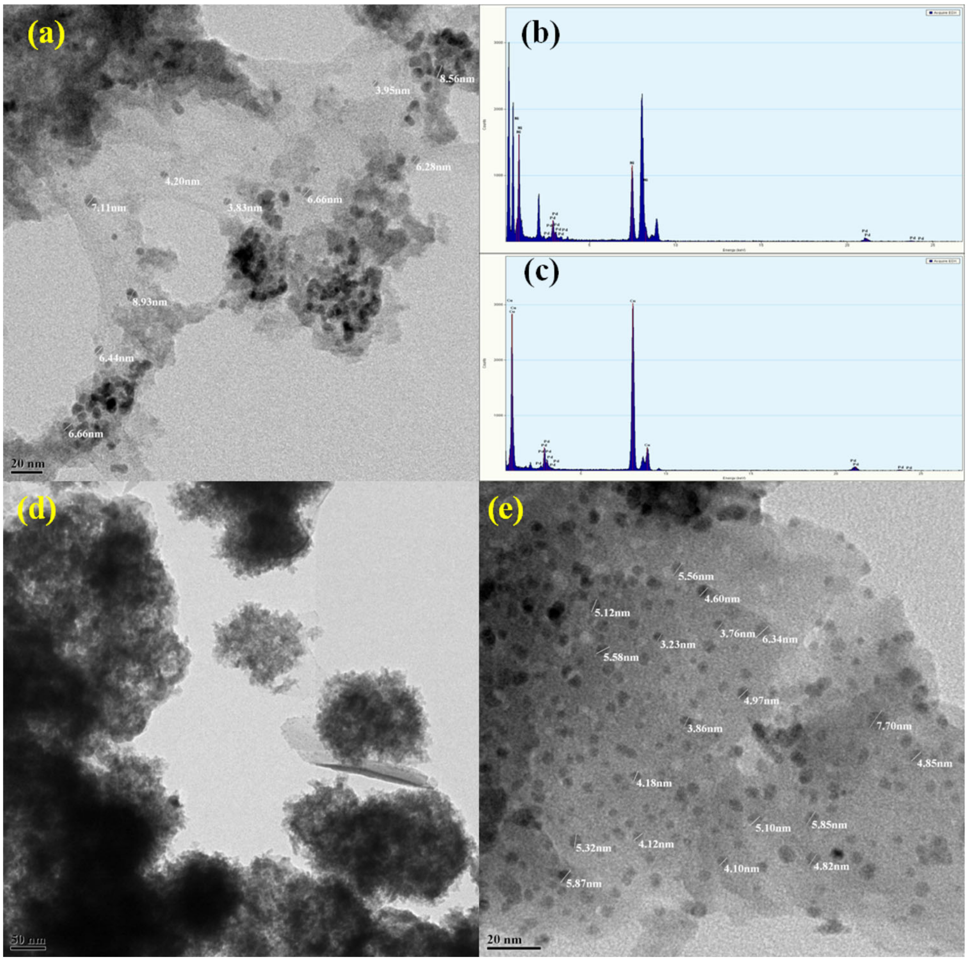


Figure 4. TEM imaging of (**a**) Pd-Ni/ABPBI (**b**) TEM-EDX of Pd-Ni/ABPBI (**c**) TEM-EDX of Pd-Cu/ABPBI (**d**) TEM images of Pd-Cu/ABPBI at 50 nm and (**e**) Particle size of Pd-Cu at 20 nm.

styrene. All reactions proceeded with E-selectivity, typical for the Mizoroki–Heck reaction. The atom economical bromide activation is a challenging task in the Mizoroki–Heck reaction and related aryl halide activation reactions. Low to moderate yields were obtained in the Mizoroki–Heck reaction of aryl bromides with Cu-Pd-ABPBI NP catalyst. The selectivity for the E-isomer was retained in these reactions also.

The reaction of 4-iodo anisole with styrene and ethyl acrylate catalyzed by Ni-Pd-ABPBI were also carried out in moderate yields (55 and 34%, respectively) in aqueous media with CTAB as surfactant.

The Suzuki coupling of various aryl iodides with several aryl boronic acids catalyzed by Ni-Pd-ABPBI proceeded in high to quantitative yields in a part aqueous solvent system of dioxane:water 1:1 (Scheme 4, Table 4). The attempted Sonogashira coupling of 4-iodo anisole with phenyl acetylene catalyzed by Ni-Pd-ABPBI catalyst, gave the alkyne Glaser type homocoupling in 92% yield.

Comparison reactions were carried out with the monometallic catalyst Pd-ABPBI. This catalyst was prepared in the similar procedure described above. Results are shown in the Tables 2, 3 and 4. The reaction of 4-iodoanisole with styrene gave 63% yield in 4.5 h (1A); The reaction of 4-bromo anisole with styrene gave 42% in 5.5 h (7A) and the Suzuki coupling of iodo benzene with benzene boronic acid gave 78% yield in 2.3 h. Overall, the monometallic catalyst gave lower yields in longer reaction times.

The reaction mechanism could be explained thus; co-ordination of nitrogen of the benzimidazole polymer to Ni followed by electron flow to Pd causes increase in electron charge density on the Pd; reducing Pd (II) to the highly active Pd (0) which then oxidatively adds to the aryl halide followed by the standard protocol of the Mizoroki–Heck reaction and finally ending with the E-substituted product. Same mechanism holds good for the high yielding Suzuki coupling. This explains the high reactivity of the bimetallic nano

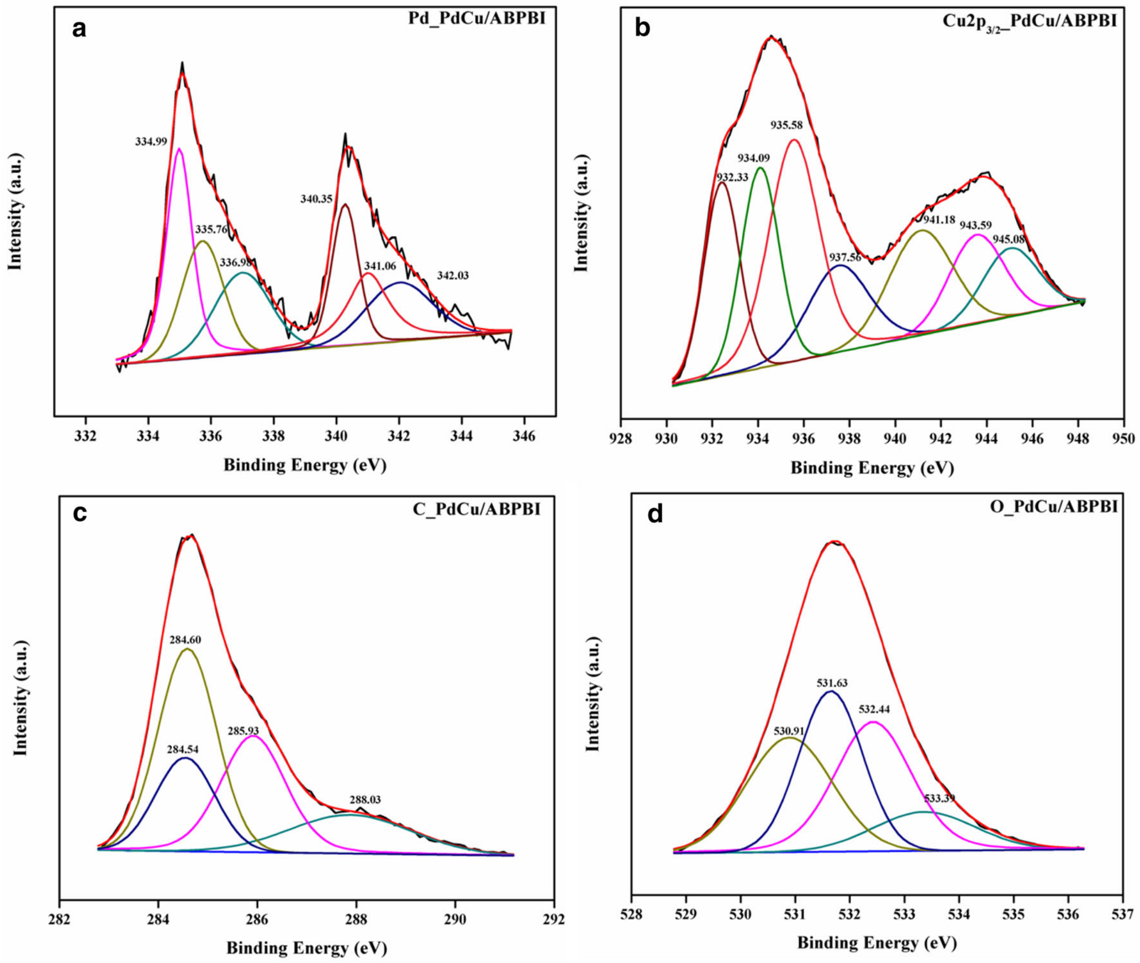


Figure 5. XPS pattern of Pd-Cu/ABPBI (**a**) Pd in Pd-Cu/ABPBI (**b**) Cu in Pd-Cu/ABPBI (**c**) Carbon in Pd-Cu/ABPBI and (**d**) Oxygen in Pd-Cu/ABPBI.

alloy supported on ABPBI polymer as well as the recyclability of the catalyst. This preliminary communication describes proof-of-concept while future work will experiment with various ratios of the bimetallic alloy to increase catalytic activity.

4. Conclusions

In summary, the bimetallic nano alloy architecture was readily constructed on the robust ABPBI polymer by operationally simple and ambient conditions. The polymer support is novel, unprecedented, extremely stable, insoluble in organic solvents and functions even at high operational temperatures without any degradation associated with phosphine ligands and other polymer supports. It is comparable with various inorganic supports like SiO_2 and Al_2O_3 in heterogeneity and the N-coordinating groups of the polymer provide excellent stabilization of the bimetallic nano particles. The harmonic Ni-Pd-ABPBI bimetallic supported nano alloy catalyst activated the Mizoroki–Heck arylation and Suzuki–Miyaura coupling in very high to quantitative yields and short reaction times. Aryl bromides gave low to moderate yields of the Mizoroki–Heck substitution products with Cu-Pd-ABPBI as catalyst. All the Mizoroki–Heck reactions proceeded with E-selectivity. Recycle of the catalyst (5 cycles) for the Mizoroki–Heck reaction of 4-iodo anisole with styrene was possible with very high yields in each cycle. Proof of concept of the novel ABPBI supported bimetallic nano alloy is demonstrated with the activation of the Mizoroki–Heck reaction and the Suzuki–Miyaura coupling. Attempted Sonogashira coupling resulted in Glaser type homo coupling of the terminal alkyne in very high yields. A variety of halide activation and other reactions to be explored yet, are now feasible with the bimetallic nano alloy heterogenized on ABPBI polymer. Further studies will elaborate on the use of this polymer supported catalysis in various organic reactions.

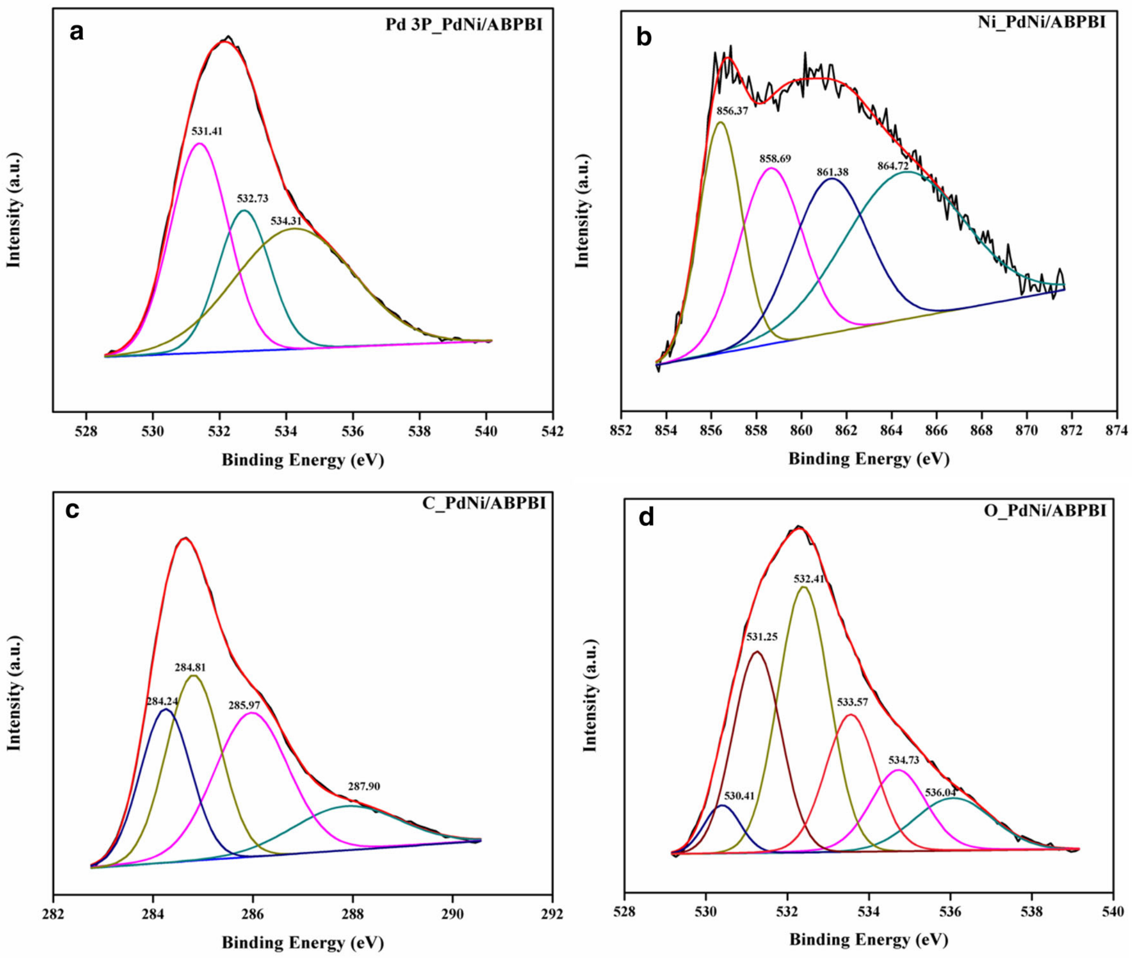
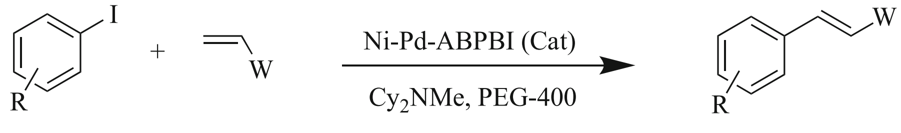


Figure 6. XPS pattern of Pd-Ni/ABPBI (**a**) Pd in Pd-Ni/ABPBI (**b**) Ni in Pd-Ni/ABPBI (**c**) Carbon in Pd-Ni/ABPBI and (**d**) Oxygen in Pd-Ni/ABPBI.



Yield : 58 - 89 %

R : H, 4-CH_3O, 4-CF_3O, 4-F, 4-Cl, 4-CH_3, 2-CH_3, 2,4-F W : $COOC_2H_5$, C_6H_5

Scheme 2. Ni-Pd–ABPBI catalysis of the Mizoroki–Heck reaction of aryl iodides.

Table 1. Ni-Pd-ABPBI catalysis of the Mizoroki–Heck reaction of aryl iodides[a].

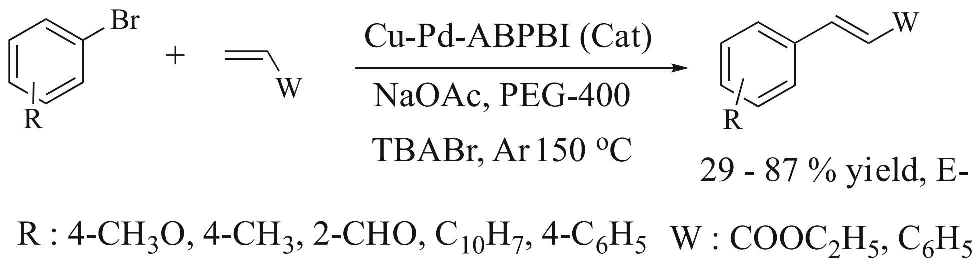
Sl. no:	Aryl Iodide	Alkene	Base, Solvent	Time h	Yield	Product, E:Z ratio
1	C_6H_5I	Ethyl acrylate	Cy_2NMe, PEG-400	1.5	75	E
2	C_6H_5I	Styrene	Cy_2NMe, PEG-400	2.5	58	E
3	$4\text{-}CH_3O.C_6H_4I$	Ethyl acrylate	NaOAc, PEG-400	2.25	66	E
4	$4\text{-}CH_3O.C_6H_4I$	Styrene	K_2CO_3, PEG-400	1.75	89	E
5	$4\text{-}CH_3O.C_6H_4I$	Styrene	Cy_2NMe, NMP	2	78	E
6	$4\text{-}CH_3O.C_6H_4I$	E-Cinnamaldehyde	NaOAc, PEG-400	16	50	E[b]
7	$4\text{-}CF_3O.C_6H_4I$	Ethyl acrylate	Cy_2NMe, PEG-400	1.10	85	E
8	$4\text{-}F.C_6H_4I$	Ethyl acrylate	Cy_2NMe, PEG-400	1.10	88	E
9	$4\text{-}Cl.C_6H_4I$	Styrene	Cy_2NMe, PEG-400	1.45	89	E
10	$4\text{-}CH_3.C_6H_4I$	Styrene	Cy_2NMe, PEG-400	1.25	86	E
11	$2\text{-}CH_3.C_6H_4I$	Styrene	Cy_2NMe, PEG-400	2.35	70	E
12	$2,4\text{-}F.C_6H_4I$	Ethyl acrylate	Cy_2NMe, PEG-400	1.10	82	E

a: Reaction conditions: ArI (1 mmol), Alkene (1–2 mmol), Cy_2NMe(1 Eq), Cat-Ni-Pd-ABPBI (0.05 g, 0.178 mmol), PEG-400, Argon, 150 °C, b: Same conditions + TBABr (1 mmol).

Table 2. Ni-Pd-ABPBI NP catalysis of Mizoroki–Heck reaction of 4-iodo anisole – Recycle study[a].

S. no	Aryl Halide	Alkene	Base, Solvent	Time h	Yield %	Product E:Z, ratio
1	$4\text{-}CH_3O.C_6H_4I$	Styrene	Cy_2NMe, PEG-400	3	89	E
1A	$4\text{-}CH_3O.C_6H_4I$	Styrene	Cy_2NMe, PEG-400	4.5	63	E[b]
2	$4\text{-}CH_3O.C_6H_4I$	Styrene	Cy_2NMe, PEG-400	7	62	E
3	$4\text{-}CH_3O.C_6H_4I$	Styrene	Cy_2NMe, PEG-400	5	97	E
4	$4\text{-}CH_3O.C_6H_4I$	Styrene	Cy_2NMe, PEG-400	2.5	80	E
5	$4\text{-}CH_3O.C_6H_4I$	Styrene	Cy_2NMe, PEG-400	4.5	83	E

a: Reaction conditions: ArI (1 mmol), Alkene (1 mmol), Cy_2NMe(1 Eq), Cat-Ni-Pd-ABPBI (0.05 g, 0.178 mmol), PEG-400, Argon, 150 °C, b: All conditions same with Monometallic catalyst – Pd-ABPBI.

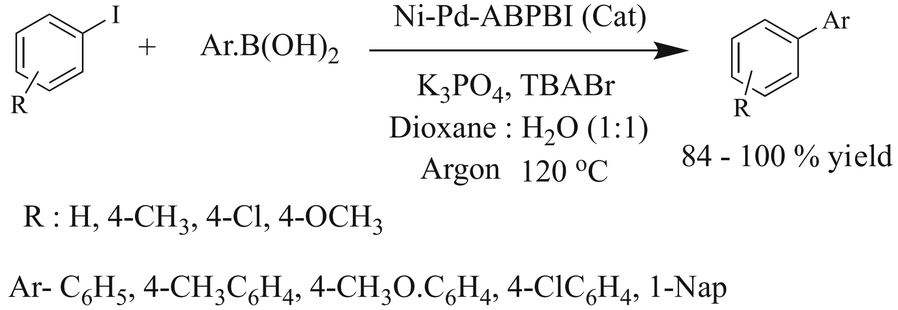


Scheme 3. Cu-Pd-ABPBI catalysis of the Mizoroki–Heck reaction of aryl bromides.

Table 3. Cu-Pd-ABPBI NP catalysis of the Mizoroki–Heck reaction of aryl bromides[a].

S. no	Aryl Halide	Alkene	Base, Solvent	Time h	Yield %	Product
1	4-$CH_3O.C_6H_4Br$	Styrene	NaOAc, DMF	72	65	E
2	4-$CH_3.C_6H_4Br$	Styrene	NaOAc, PEG-400	1.5	35	E
3	4-$CH_3.C_6H_4Br$	Ethyl acrylate	Cy_2NMe, PEG-400	3.15	28	E
4	2-$CHO.C_6H_4Br$	Styrene	NaOAc, PEG-400	7.25	87	E
5	1-Br-Nap	Styrene	NaOAc, PEG-400	5	74	E
6	1-Br-Nap	Ethyl acrylate	NaOAc, PEG-400	12	33	E
7	4-$CH_3O.C_6H_4Br$	Styrene	NaOAc, PEG-400	9.5	59	E
7A	4-$CH_3O.C_6H_4Br$	Styrene	NaOAc, PEG-400	5.5	42	E[b]
8	4-$CH_3O.C_6H_4Br$	Styrene	NaOAc, NMP	28	29	E
9	4-$CH_3O.C_6H_4Br$	Styrene	NaOAc, PEG-200	28	37	E
10	4-Br-Biph	Styrene	NaOAc, PEG-400	19	45	E
11	4-$CH_3.C_6H_4Br$	Styrene	NaOAc, PEG-400	1.5	35	E
12	4-$Cl.C_6H_4Br$	Styrene	NaOAc, PEG-400	2	25	E

[a]Reaction conditions: ArBr (1 mmol), Alkene (1–2 mmol), NaOAc (1 Eq), TBABr (1 mmol), Cat-Cu-Pd-ABPBI (0.05 g, 0.175 mmol), PEG-400, Argon, 150 °C, b: All conditions same with Monometallic catalyst – Pd-ABPBI.



Scheme 4. Ni-Pd-ABPBI catalysis of the Suzuki coupling of aryl iodides.

Table 4. Ni-Pd-ABPBI NP catalysis of the Suzuki coupling of aryl iodides[a].

S. no	Aryl Halide	Aryl boronic acid	Product	Time h	Yield %
1	C_6H_5I	$C_6H_5B(OH)_2$	$C_6H_5.C_6H_5$	2	87
1A	C_6H_5I	$C_6H_5B(OH)_2$	$C_6H_5.C_6H_5$	2.30	78[b]
2	C_6H_5I	4-$CH_3O.C_6H_4B(OH)_2$	4-$CH_3O.C_6H_4.C_6H_5$	2.5	84
3	4-$CH_3.C_6H_4I$	$C_6H_5B(OH)_2$	4-$CH_3.C_6H_4.C_6H_5$	2	94
4	4-$CH_3.C_6H_4.I$	4-$Cl.C_6H_4B(OH)_2$	4-$Cl.C_6H_4.C_6H_4.CH_3$-4′	2.5	95
5	4-$Cl.C_6H_5.I$	$C_6H_5B(OH)_2$	4-$Cl.C_6H_4.C_6H_5$	1.5	100
6	4-$Cl.C_6H_4.I$	4-$CH_3.C_6H_4B(OH)_2$	4-$Cl.C_6H_4.C_6H_4.CH_3$-4′	2	100
7	4-$CH_3O.C_6H_4I$	$C_6H_5B(OH)_2$	4-$CH_3O.C_6H_4.C_6H_5$	2.15	100
8	4-$CH_3O.C_6H_4I$	4-$CH_3O.C_6H_4B(OH)_2$	4-$CH_3O.C_6H_4.C_6H_4.OCH_3$-4′	2	92
9	4-$CH_3O.C_6H_4I$	1-Nap-$B(OH)_2$	1-Nap-$C_6H_4.OCH_3$-4	1.5	100
10	4-$CH_3O.C_6H_4I$	$C_6H_5B(OH)_2$	4-$CH_3O.C_6H_4.C_6H_5$[b]	2	98

a-Reaction conditions: ArI (0.5 mmol), Aryl boronic acid (0.6 mmol), TBABr (0.5 mmol), K_3PO_4 (0.6 mmol), Cat-Ni-Pd-ABPBI (0.025 g, 0.089 mmol), dioxane:water 1:1 (10 mL), Argon, 120 °C; b-All conditions same with Monometallic Catalyst Pd-ABPBI, b-Same reaction conditions with Catalyst Cu-Pd-ABPBI (0.025 g, 0.0875 mmol).

Supplementary Information (SI)

Supplementary information is available at www.ias.ac.in/chemsci.

Acknowledgements

UKK thanks the BRNS for financial support, project GAP-319326 and VPP a PA-II post. We also thank Dr. CV Rode for assistance with the catalyst characterization.

Conflict of interest There are no conflicts to declare.

References

1. Sinfelt J H 1983 *Bimetallic catalysts: Discoveries, concepts and applications* (New York: John Wiley & Sons)
2. Polshettiwar V and Asefa T 2013 *Nanocatalysis: Synthesis and Applications* (Hoboken, New Jersey: John Wiley & Sons)
3. Son S U, Jang Y, Park J, Na H B, Park H M, Yun H J, Lee J and Hyeon T 2004 Designed synthesis of atom-economical Pd/Ni bimetallic nanoparticle-based catalysts for sonogashira coupling reactions *J. Amer. Chem. Soc.* **126** 5026
4. Feng L, Chong H, Li P, Xiang J, Fu F, Yang S, Yu H, Sheng H and Zhu M 2015 Pd–Ni alloy nanoparticles as effective catalysts for Miyaura–Heck coupling reactions *J. Phys. Chem.* **119** 11511
5. Rai R K, Tyagi D, Gupta K and Singh S K 2016 Activated nanostructured bimetallic catalysts for C–C coupling reactions: recent progress *Catal. Sci. Technol.* **6** 3341
6. Reetz M T, Breinbauer R and Wanninger K 1996 Suzuki and Heck reactions catalyzed by preformed palladium clusters and bimetallic clusters *Tetrahedron Lett.* **37** 4499
7. Thathagar B M B, Beckers J and Rothenberg G 2003 Combinatorial design of copper based mixed nanoclusters: New catalysts for Suzuki cross-coupling *Adv. Synth. Catal.* **345** 979
8. Kyriakou G, Boucher M B, Jewell A D, Lewis T J, Lawton T J, Baber A E, Tierney H L, Flytzani-Stephanopoulos M and Sykes E C H 2012 Isolated metal atom geometries as a strategy for selective heterogeneous hydrogenations *Science* **335** 1209
9. Sustmann R, Hopp P and Holl P 1989 Reactions of organic halides with olefins under Ni (0)-catalysis. Formal addition of hydrocarbons to CC-double bonds *Tetrahedron Lett.* **30** 689
10. Kelkar A A, Hanoka T, Kubota Y and Sugi Y 1994 The vinylation of bromobiphenyls using homogeneous nickel catalysts *Catal. Lett.* **29** 69
11. Iyer S, Ramesh C and Ramani A 1997 Ni(0) catalyzed reactions of aryl and vinyl halides with alkenes and alkynes *Tetrahedron Lett.* **38** 8533
12. Iyer S, Ramesh C, Sarkar A and Wadgaonkar P P 1997 The vinylation of aryl and vinyl halides catalyzed by copper salts *Tetrahedron Lett.* **38** 8113
13. Iyer S and Thakur V V 2000 The novel use of Ni, Co, Cu and Mn heterogeneous catalysts for the Heck reaction *J. Mol. Catal. A Chem.* **157** 275
14. Handa S, Slack E D and Lipshutz B H 2015 Nanonickel-catalyzed Suzuki–Miyaura cross-couplings in water *Angew. Chem. Int. Ed.* **54** 11994
15. Yao Q, Kinney E P and Yang Z 2003 Ligand-free Heck reaction: $Pd(OAc)_2$ as an active catalyst revisited *J. Org. Chem.* **68** 7528
16. Bozell J J and Vogt C E 1988 Bimetallic catalysis. A new method for the activation of chloroarenes toward palladium-catalyzed coupling with olefins *J. Amer. Chem. Soc.* **110** 2655
17. Sarkar S M, Uozumi Y and Yamada Y M A 2011 A highly active and reusable self-assembled poly(imidazole/palladium) catalyst: Allylic arylation/alkenylation *Angew. Chem. Int. Ed.* **50** 9437
18. Molnar A 2013 *Palladium Catalyzed Coupling Reactions: Practical Aspects and Future Developments* (Hoboken, New Jersey: John Wiley & Sons)
19. Kann N 2010 Recent applications of polymer supported organometallic catalysts in organic synthesis *Molecules* **15** 6306
20. Wan B-S, Liao S-J, Xu Y and Yu D-R 1998 Polymer-supported palladium–nickel bimetallic catalyst for the regioselective hydroesterification of styrene *J. Mol. Catal. A Chem.* **136** 263
21. Liu C, Xu Y, Liao S and Yu D 1999 Synergic effect of polymer-supported bimetallic catalysts in the hydrogenation and isomerization of 1-octene *J. Mol. Catal. A Chem.* **149** 119
22. Wan B, Liao S and Yu D 1999 Polymer-supported palladium–manganese bimetallic catalyst for the oxidative carbonylation of amines to carbamate esters *Appl. Catal. A Gen.* **183** 81
23. Udumula V, Tyler J H, Davis D A, Wang H, Linford M R, Minson P S and Michaelis D J 2015 Dual optimization approach to bimetallic nanoparticle catalysis: Impact of M1/M2 ratio and supporting polymer structure on reactivity *ACS Catal.* **5** 3457
24. Seth K, Purohit P and Chakraborti A K 2014 Cooperative catalysis by palladium–nickel binary nanocluster for Suzuki–Miyaura reaction of ortho-heterocycle-tethered sterically hindered aryl bromides *Org. Lett.* **16** 2334
25. Ohtaka A, Sansano J M, Najera C, Miguel-Garcia I, Berenguer-Murcia A and Cazorla-Amoros D 2015 Palladium and bimetallic palladium–nickel nanoparticles supported on multiwalled carbon nanotubes: application to carbon–carbon bond-forming reactions in water *ChemCatChem.* **7** 1841
26. Kumbharkar S C and Kharul U K 2010 New N-substituted ABPBI: Synthesis and evaluation of gas permeation properties *J. Membrane Sci.* **360** 418
27. Chen Z, Yu X and Song Y 2016 Palladium nanoparticle supported on mesoporous polybenzimidazole as a heterogeneous catalyst for Suzuki cross-coupling reaction in aqueous media *Ferroelectrics* **494** 200
28. Whitcombe N J, Hii K K and Gibson S E 2001 Advances in the Heck chemistry of aryl bromides and chlorides *Tetrahedron* **57** 7449

29. Feng Y-S, Lin X-Y, Hao J and Xu H-J 2014 Pd–Co bimetallic nanoparticles supported on graphene as a highly active catalyst for Suzuki–Miyaura and Sonogashira cross-coupling reactions *Tetrahedron* **70** 5249
30. Lu P, Teranishi T, Asakura K, Miyake M and Toshima N 1999 Polymer protected Ni/Pd bimetallic nano clusters: Preparation, characterization and catalysis for hydrogenation of nitrobenzene *J. Phys. Chem. B* **103** 9673
31. Luo W, Sankar M, Beale A, He Q, Kiely C, Bruijnincx P C A and Weckhuysen B M 2015 High performing and stable supported nano-alloys for the catalytic hydrogenation of levulinic acid to γ-valerolactone *Nat. Commun.* **6** 6540
32. Shit S C, Singuru R, Pollastri S, Joseph B, Rao B S, Lingaiah N and Mondal J 2018 Cu–Pd bimetallic nanoalloy anchored on a N-rich porous organic polymer for high performance hydrodeoxygenation of biomass-derived vanillin *Catal. Sci. Tech.* **8** 2195
33. Abdolmaleki A and Molavian M R 2015 Synthesis and characterization of poly(benzimidazole-amide)/Ni nanocomposite based on 2,6-Bis(2-benzimidazol-2-yl)pyridine moiety *Comp. Inter.* **22** 203
34. Mane R B, Hengne A M, Ghalwadkar A A, Vijayanand S, Mohite P H, Potdar H S and Rode C V 2010 Cu:Al nano catalyst for selective hydrogenolysis of glycerol to 1,2-propanediol *Catal. Lett.* **135** 141