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1 2	Metallosurfactant based Pd-Ni Alloy Nanoparticles as proficient catalyst in Mizoroki Heck Coupling Reaction
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### 1 Abstract

A highly efficient, operationally simple and green catalytic approach involving Pd-Ni alloy 2 nanoparticles (NPs) has been developed using microwaves (MW) as an energy source and water-3 ethanol as a solvent system. Metallosurfactants were synthesized and used as precursors to 4 fabricate Pd-Ni alloy NPs with a good control over the size and morphology. Surfactant capped 5 zerovalent Pd-Ni alloy NPs were fabricated in the metallomicellar cores by a two-phase 6 reduction method. The synthesized NPs exhibited the highest catalytic efficiency for the 7 stereoselective Mizoroki Heck coupling featuring short reaction time, mild reaction conditions, 8 9 wide substrate scope, preclusion of toxic organic solvents, easy recovery and recyclability of the 10 catalyst.

Keywords: Pd-Ni alloy nanoparticles, Mizoroki Heck coupling, Microwave, Green chemistry

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### 1 1. Introduction

Catalysis is a useful tool in the area of synthetic chemistry for performing classical 2 reactions under milder conditions with dramatically enhanced yields in lesser reaction times.<sup>1</sup> In 3 the present era, where every catalytic approach is critically examined in terms of activity and 4 selectivity, the environment-friendly aspect is much more emphasized due to global 5 environmental concerns.<sup>2</sup> Thus, the quest for a cleaner, simpler and greener approach has 6 underscored the need for developing sustainable and environment-friendly strategies.<sup>3</sup> The 7 search for such catalytic systems has led to the advent of nanocatalysts, which amalgamate the 8 superior selectivity of homogeneous catalysts with the recyclability of heterogeneous catalysts.<sup>4-6</sup> 9 The distinct properties exhibited by nanoparticles (NPs) over their bulk analogues are mainly 10 attributed to quantum effects and surface effects, i.e. smaller particle size leads to a larger surface 11 area to volume ratios providing more number of active atoms on the surface.<sup>7-9</sup> Out of various 12 classes of nanomaterials, bimetallic NPs owing to their diverse applications have attracted many 13 scientists as they not only promise bifunctional performance of the two constituting metals but 14 also impart additional properties such as strength, functionality, and stability.<sup>10-14</sup> These smartly 15 engineered nanomaterials with a remarkable catalytic activity empower synthetic chemists to 16 switch from previously existing protocols to achieve desired goals while addressing economic 17 and environmental challenges.<sup>15-16</sup> 18

The catalytic significance of a cheaper transition metal elements in a number of organic 19 syntheses <sup>17-18</sup> has prompted scientists to develop cost-effective systems that combine their 20 excellent catalytic properties with another noble metals, such as palladium (Pd), for applications 21 in sensor design,<sup>19</sup> fuel cells,<sup>20</sup> catalysis,<sup>21</sup> and electrocatalysis.<sup>22</sup> Owing to its higher efficiency 22 and selectivity as a catalyst, Pd is majorly known for its utility in organic syntheses particularly 23 in C-C bond formations, e.g. Mizoroki Heck Coupling and Suzuki-Miyaura Coupling reactions,<sup>23</sup> 24 which received acknowledgment as Noble Prize award (2010) in chemistry. The earlier reports 25 for Pd-based homogeneous catalysis <sup>24-26</sup> suffered from a number of drawbacks such as toxicity, 26 high cost, and product contamination. These drawbacks paved the way to the application of Pd-27 based NPs as they performed equally well in environment-friendly constraints with no significant 28 metal leaching.<sup>27-30</sup> Bimetallic NPs are of great significance among all the Pd-based catalysts as 29 they account for high catalytic activity with lesser Pd content.<sup>31-34</sup> 30

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Keeping in view the industrial significance of Mizoroki Heck coupling, the present work 1 was intended to develop a new catalytic system comprising of Pd-Ni alloy NPs that not only 2 ensure the synergistic effect of two constituting metals but also redresses the economic and 3 environmental issues. The as-fabricated catalytic system addresses all the challenges of current 4 solution based co-reduction methods of synthesis, i.e. size and growth control etc. Instead of 5 using simple metal salts as precursors and surfactants. Pd-Ni allov NPs have been synthesized 6 following two-phase reduction of mixed reverse metallomicelles formed from Pd and Ni 7 metallosurfactants (complex 1 and 2) which resulted in NPs with good control over size and 8 morphology. The as-synthesized catalyst was critically screened for its efficiency in conditions 9 fitting the Green Chemistry frame. The green chemistry principles primarily account for the 10 promotion of aqueous reaction media, preclusion of toxic conventional organic solvents and 11 incorporation of efficient energy input sources.<sup>35-39</sup> The efficiency of MW over traditional oil-12 bath heating<sup>40</sup> prompted us to perform the well-exploited Mizoroki Heck coupling reaction with 13 Pd-Ni NPs as catalysts under microwave (MW) conditions in the environmentally benign 14 aqueous solvent system (water/ethanol) and to the best of our knowledge, no report has been 15 listed in the literature using Pd-Ni alloy NPs under the aforementioned conditions for Mizoroki 16 Heck coupling. 17

### 18 2. Experimental Section

### 19 2.1. Chemicals

Palladium(II) Chloride (99%), dodecylamine (98.6%), nickel(II) chloride (99%), sodium 20 borohydride, NaBH<sub>4</sub> (99%) and haloarenes (99%) were purchased from Sigma-Aldrich. Styrene 21 22 (99%) was purchased from TCI and absolute ethanol (99.9%) was purchased from Changshu Yuang. Dimethylformamide (DMF) was dried with matrix molecular sieves 5 Å, 30-40 mesh 23 supplied by Sigma-Aldrich. Dichloromethane (DCM), potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) sodium 24 carbonate (Na<sub>2</sub>CO<sub>3</sub>) sodium bicarbonate (NaHCO<sub>3</sub>), potassium bicarbonate (KHCO<sub>3</sub>), sodium 25 hydroxide (NaOH) and potassium hydroxide (KOH) were purchased from Fischer Scientific and 26 all the aqueous solutions were prepared with double distilled water. 27

### 28 2.2. Instrumentation

The X-ray diffraction (XRD) spectra were recorded on a Panalytical X'Pert Pro X-ray
diffractometer equipped with Cu-Kα radiation (1.5406 Å) operating at 40 kV, with a scanning

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speed of 8°/min to examine the crystalline phase of NPs. UV-Visible spectra were recorded with

Evolution 160 UV-Vis operated in the range 200-800 nm using quartz cuvettes of path length 1

cm. Infrared (IR) spectroscopic studies were carried out using Perkin Elmer-FTIR Spectrum-100 3 operated in spectral domain of 400 to 4000 cm<sup>-1</sup>. High resolution transmission electron 4 microscopy (HRTEM) studies were performed on FP 5022/22-Tecnai G2 20 S-TWIN operated 5 at an accelerating voltage of 200 kV. Field emission scanning electron microscopy (FESEM) was 6 executed on Hitachi (SU8010) operated at an accelerating voltage of 15.0 kV. The chemical 7 composition of the synthesized NPs was confirmed by energy dispersive X-ray spectroscopy 8 (EDX) along with mapping using Philips XL 30 EDS unit. X-ray photoelectron spectroscopy 9 (XPS) was performed on ESCA+, (omicron nanotechnology, Oxford Instrument Germany) 10 equipped with monochromator aluminum source (Al k $\alpha$  radiation hv = 1486.7 eV). The 11 instrument was operated at 15 kV and 20mA. Samples in powder form were deposited on Cu 12 tape and degassed for overnight in XPS FEL chamber to minimize the air contamination at 13 sample surface as well as in the main chamber. To overcome the charging problem a charge 14 neutralizer of 2 keV was applied and binding energy of C1s core (284.6eV) was taken as 15 reference. The atomic weight % of Pd in the optimized catalytic dose was assessed by ICP-AES 16 analysis performed on ICP-OES Varian 720-ES. ICP-MS analyses were done on ICP-MS 17 Agilent 7800 to know the leached Pd concentration. The Mizoroki Heck coupling reactions were 18 performed on the commercial microwave, Multiwave Pro by Anton Paar equipped with infrared 19 temperature control system in sealed tubes. <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on a model 20 advance II (Bruker) instrument with a frequency 400 MHz for <sup>1</sup>H NMR and a frequency of 100 21 MHz frequency for <sup>13</sup>C NMR using TMS as the internal standard and chloroform (CDCl<sub>3</sub>) as the 22 solvent. 23

# 24 2.3. Synthesis of Pd and Ni precursors

Metallosurfactants, bisdodecylamine palladium (II) chloride (complex 1) and bisdodecylamine nickel (II) chloride (complex 2) were used as precursors of Pd and Ni (NPs), respectively and were synthesized by ligand insertion method as per the synthesis earlier reported by our group.<sup>42-<sup>43</sup> For complex 1, palladium chloride salt and the ligand, dodecylamine ( $C_{12}H_{25}NH_2$ ) were taken in 1:2 ratio and heated at 60 °C using dry N,N-dimethylformamide (DMF) as a solvent under</sup>

30 vigorous stirring for 3 h. The double chained metallosurfactant (complex 1) thus formed was

recrystallized using ethanol (EtOH) and vacuum dried before further use. Similarly, complex 2
 was synthesized using nickel chloride salt under above-mentioned conditions (Scheme 1, ESI).

### 2.4. Synthesis of Pd-Ni NPs

Equimolar solutions (0.4 mM) of each of Pd and Ni precursors were prepared separately in a 4 5 given volume (10 mL) of dichloromethane (DCM) and were mixed well by stirring to give a uniform solution (S). The metallosurfactant solutions were prepared above their critical micelle 6 concentration (CMC). This ensured the formation of reverse micelles in the presence of an 7 organic medium in which metal heads were present in the micellar core in +2 oxidation state. 8 These metal ions were then reduced by following a two-phase redox methodology. An aqueous 9 solution of sodium borohydride (40 mM, 40 mL) was freshly prepared and added instantaneously 10 to the solution, S. High reductant to the metallosurfactant molar ratio (20:1) resulted in an 11 12 immediate reduction of metal ions in +2 oxidation state to a zerovalent metallic state. The black coloured NPs thus formed in the organic phase was separated using a separatory funnel and 13 14 vacuum-dried further.

## 15 2.5. Catalytic application of Pd-Ni NPs in Mizoroki Heck coupling reaction

In a typical experiment, styrene (1 mmol), haloarene (1 mmol), base (1.5 mmol), solvent (2 mL) 16 and catalyst (10 mg, 0.35 mol% Pd) were sealed in a tube and subjected to MW at 300 W (120 17 <sup>o</sup>C) (Scheme 1). The different batch experiments were performed in sealed tubes for fixed run 18 19 time and progress of the reaction in each batch was monitored by thin layer chromatography (TLC). The comparison of TLC plates of reaction mixture for each run time gave idea about the 20 21 time of reaction completion. It is to be noted that the run-time for each batch reaction includes the heat up and hold times in MW after which the MW are shut off and the reaction cooled to 22 room temperature from same target temperature in all the runs. Once the reaction was over, the 23 catalyst was separated from the reaction mixture by centrifugation followed by dilution of 24 remaining solution with water. The product was extracted with diethyl ether and dried over 25 sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>). After ether evaporation, recrystallization of product was done in 26 ethanol. The reaction conditions were optimized by varying different factors such as solvent, 27 base and catalyst amount to find out the best combination that leads to faster reaction with good 28 product yield. 29

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Scheme 1: Mizoroki Heck coupling reaction between styrene and haloarenes under MW conditions (300 W, 120 °C).

### 4 **3. Results and Discussion**

# 5 3.1. Synthesis and characterization of Pd-Ni NPs

The complex 1 and 2 which are double chained metallosurfactants of Pd and Ni form reverse 6 micelles in DCM. The strong solvophilic interactions between hydrocarbon tails of 7 metallosurfactant and organic solvent push the metal heads in core whereas the hydrocarbon tails 8 are present as shell.<sup>41-42</sup> The metal ions present in the core of micelles were subsequently reduced 9 to form zerovalent metal atoms by using NaBH<sub>4</sub> as a reducing agent. The use of a strong 10 reducing agent causes instantaneous reduction of both metal ions present in the micellar core. It 11 is proposed that both metals nucleate in a restricted core size where one metal diffuses into the 12 lattice of another forming an alloy structure. The growth of nuclei, thus formed, is controlled by 13 14 the surfactant chains (dodecylamine), present in precursor molecules, which subsequently get physically adsorbed on the NPs surface (Fig. S1, ESI). 15

The alloy structure was elucidated by characterization of as-synthesized Pd-Ni NPs. The UV-Vis spectra of complex 1, 2 and Pd-Ni NPs (recorded in DCM) are given in Fig. S2(a) (ESI). It can be seen that the characteristic absorption peaks of complex 1 and 2 were completely absent in the broad continuous absorption spectrum of Pd-Ni NPs confirming a complete reduction of bivalent metal ions to zerovalent nanoalloys.<sup>41-42</sup>

TEM reveals well dispersed Pd-Ni NPs of spherical shape with average 5 nm (Fig. 1(a)). The different contrast in HRTEM image confirmed the formation of bimetallic NPs. The dspacing between lattice planes is found to be 2.11 Å, which is consistent with the alloy structure of Pd-Ni NPs (Fig. S2(b), ESI).<sup>43</sup> XRD pattern of Pd-Ni NPs shows a broad peak at  $2\theta = 41.8^{\circ}$ , which is placed in between the peaks corresponding to (111) plane of pure Pd (40.1°) and Ni (44.4°). The shift in peak position suggested that Ni has entered the lattice structure of Pd (Fig.

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1(b)) thereby confirming the formation Pd-Ni alloy NPs. The only prominent diffraction peak 1 corresponding to (111) suggests anisotropic growth of NPs along (111) direction.<sup>44</sup> The EDX 2 spectrum of the sample showed that the synthesized NPs contained Pd and Ni in almost 1:1 3 atomic ratio and were free of impurities (Fig. S2(c), ESI). FESEM was performed to gain insight 4 into the morphology of the synthesized NPs. The image, (Fig. 1(c)), reveals a nearly spherical 5 morphology of NPs with a slight agglomeration with a particle size in the range of 10-15 nm. 6 Elemental maps of the region selected from FESEM images, highlighting Pd and Ni metals with 7 different colours, indicate the homogeneous distribution of metals thereby supporting the alloy 8 nature of the synthesized NPs (Fig. S3, ESI). 9

Further, stabilization of NPs by surfactant, dodecylamine, was confirmed by FTIR 10 spectroscopy. FTIR spectrum of surfactant stabilized NPs shows a significant shift in -NH 11 stretching frequencies as compared to that of a pure dodecylamine (Fig. 1(d)). Compared to pure 12 dodecylamine, the NH asymmetric stretching vibrations in dodecylamine stabilized NPs show a 13 frequency shift of 21 cm<sup>-1</sup> and are observed at 3317 cm<sup>-1</sup>. The NH symmetric stretching band 14 also shifts from 3182 cm<sup>-1</sup> to 3084 cm<sup>-1</sup>. This is attributed to the surface adsorption of 15 dodecylamine on NPs through -NH<sub>2</sub> group resulting in shift of stretching bands to lower 16 frequencies. 17



Fig. 1: (a) TEM image (b) XRD pattern (c) FESEM image and (d) FTIR spectrum of Pd-Ni NPs

To further know the surface electronic structure, XPS analysis was done for as-3 synthesized NPs. The spectra exhibit signals corresponding to binding energies (BE) of Pd, Ni, N 4 5 and C marking their presence on NP surface. Narrow Pd 3d region shows two peaks at 335.8 eV and 341.2 eV for Pd  $3d_{5/2}$  and  $3d_{3/2}$ , respectively (Fig. 2(a)). These signals for Pd in Pd-Ni alloy 6 NPs are found to be shifted to higher BE values as compared to pure Pd signals (335.2 eV and 7 340.5 eV) indicating the modified electronic structure of Pd in alloyed state. Alloying of Pd and 8 9 Ni causes the down shift of Pd's d-band centre with respect to Fermi level causing higher BE values. The two peaks observed at 853.3 eV and 870.4 eV correspond to Ni  $2p_{3/2}$  and  $2p_{1/2}$  states, 10 respectively (Fig. 2(b)).<sup>45</sup> The small satellite peaks (at ~6 eV and 3eV) may be due to small % of 11 surface oxidized Ni.<sup>46</sup> The BE peaks at 399.5 eV and 285.0 eV (Fig. 2(c) and 2(d)) correspond to 12 N 1s and C 1s present in dodecylamine moieties attached to surface of NPs.<sup>47</sup> 13

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Fig. 2 XPS regions for (a) Pd (b) Ni (c) N (d) C.

### 3.2. Catalytic application of Pd-Ni NPs in Mizoroki Heck coupling reaction

The model reaction between styrene and iodobenzene was performed with different solvents 4 using  $K_2CO_3$  as a model base. Figure 3(a) shows results from the aforementioned reaction 5 performed in different solvents (H<sub>2</sub>O, EtOH, EtOH-H<sub>2</sub>O mixture, DMF, DCM) and solvent-free 6 condition. Solvent screening showed that in MW conditions water-ethanol solvent mixture is as 7 competent as the organic solvent DMF. Despite the low solubility of substrates in water, the 8 exceptional performance of this greener water based solvent mixture can be attributed to its 9 microwave absorption efficiency together with EtOH as a co-solvent that resolves the solubility 10 issues of substrates. The water-EtOH mixture having a higher microwave absorptivity (measured 11 as tan  $\delta$  value) in combination, leads to an efficient conversion of MW into heat.<sup>48</sup> Apart from 12 the environment-friendly aspect of water-EtOH solvent mixture, the ease of product separation 13 14 from the solvent mixture at ambient temperature advocates the use of water-EtOH mixture over conventional organic solvents such as DMF. 15

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Fig. 3: Effect of (a) solvent in presence of K<sub>2</sub>CO<sub>3</sub> (1.5 mmol) as base (b) base in Water/EtOH 6:4
(2 ml) as solvent on coupling reaction between styrene and iodobenzene.

On the basis of above-optimized conditions, the coupling reaction performed with MW, 10 was analyzed for reaction time and catalyst dose optimization (Fig. 4). Figure 4(a) shows the 11 effect of reaction time on % yield of the product in subsequent experiments under MW 12 conditions. It is to be noted that separate experiments were performed for fixed times and as 13 monitored by TLC, the reaction was complete in 8 minutes with 87% yield, with no significant 14 increase in the yield on increasing the reaction time. The catalyst amount was optimized by 15 performing the reaction with different amount of catalyst. No reaction occurred in the absence 16 of catalyst, however, the product yield increased significantly with increase in the amount of 17 catalyst till 8 mg (Fig. 4(b)). A further increase in the catalyst amount did not show any 18 significant change in the product yield. Hence, the optimum amount of the synthesized catalyst 19 (Pd-Ni NPs) was fixed at 8 mg (7.76 wt% and 0.28 mol% Pd). The performance of the catalyst 20 was also assessed using conventional heating source under sealed conditions and the results, in 21 22 terms of % yield of product, are depicted in Fig. 5.

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Reaction conditions: Styrene (1 mmol), Iodobenzene (1 mmol), K<sub>2</sub>CO<sub>3</sub> (1.5 mmol), Water/EtOH 6:4 (2 ml), MW, sealed tubes, Temperature 120 °C.

Fig. 4: Effect of (a) different run times of reaction at fixed catalyst dose (10 mg) and (b) catalyst amount on % yield of coupling product.



6 7 Reaction conditions: Styrene (1 mmol), Iodobenzene (1 mmol), K<sub>2</sub>CO<sub>3</sub> (1.5 mmol), Water/EtOH 6:4 (2 ml), 8 conventional oil bath heating conditions, sealed tubes, 120 °C.

Fig. 5: % Yield of coupling product for different run times under sealed tube conditions with 9 conventional heating source. 10

It is not possible to clearly compare the catalysts' performance under two energy sources since 11 the temperature profile and reaction conditions achieved in either case were not exactly 12 identical. The reason for such difference in temperature profiles of reaction performed under 13

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conventional heating and MW lies in the mechanisms of heat transfer. While the reaction 1 system achieves the desired temperature through conduction-convection mechanism in 2 conventional heating source, the heat transfer mechanism in MW is based on radiative losses on 3 account of rotational-vibrational motion of molecules. It is noteworthy that NPs also add to the 4 microwave absorbing capacity of the catalytic system which is evident through the temperature 5 profiles of blank solvent system and system containing NPs (Fig. S4, ESI) that in presence of 6 NPs, the temperature is achieved faster. The superficially heated catalytic surfaces add to 7 efficiency of heterogeneous catalytic system<sup>49</sup> comprising of NPs when employed in 8 concomitance with MW, which is an operationally easier method to achieve desired temperature 9 conditions in shorter times. 10

Next, we checked the catalytic system for its substrate scope. Table 1 shows the % yield
of the cross-coupled products of alkene sources (styrene and ethyl acrylate) with various
substituted aryl halides (scheme 2).



 $X = I, Br, Cl; R = H, 4-OCH_2, 4-NO_2, 4-CN, 4-COCH_3; Z = Ph (styrene), COOCH_2CH_3 (ethyl acrylate)$ 

Scheme 2: Mizoroki Heck coupling between alkenes and substituted aryl halides

 Table 1: Mizoroki Heck cross-coupling reaction between alkene and different substituted aryl halides.\*

S. No.	Z	Х	R	Yield (%) <sup>a</sup>
1.	Ph	Ι	Н	88
2.	Ph	Br	Н	85
3.	Ph	Br	p-OCH <sub>3</sub>	85
4.	Ph	Br	p-NO <sub>2</sub>	86
5.	Ph	Br	p-CN	84
6.	Ph	Cl	H	82
7.	Ph	Cl	p-NO <sub>2</sub>	83
8.	Ph	Cl	p-COCH <sub>3</sub>	81
9.	COOCH <sub>2</sub> CH <sub>3</sub>	Ι	H	87
10.	COOCH <sub>2</sub> CH <sub>3</sub>	Br	Н	86
11.	COOCH <sub>2</sub> CH <sub>3</sub>	Br	p-OCH <sub>3</sub>	84
12.	COOCH <sub>2</sub> CH <sub>3</sub>	Br	p-NO <sub>2</sub>	85
13.	COOCH <sub>2</sub> CH <sub>3</sub>	Br	p-CN	85

14.	COOCH <sub>2</sub> CH <sub>3</sub>	Cl	Н	82
15.	COOCH <sub>2</sub> CH <sub>3</sub>	Cl	p-NO <sub>2</sub>	83
16.	COOCH <sub>2</sub> CH <sub>3</sub>	Cl	p-COCH <sub>3</sub>	80

\*Reaction conditions: Styrene/ Ethyl acrylate (1 mmol), aryl halide (1 mmol), K<sub>2</sub>CO<sub>3</sub> (1.5 mmol), Water/EtOH 6:4 (2 ml), Microwave (300 W), Temperature 120 °C, 10 mins, <sup>a</sup> Yield of isolated product

Further, the catalyst (Pd-Ni NPs) was checked for its recyclability by recovering it
through centrifugation. The recovered catalyst was washed with ether followed by drying in air.
The catalytic performance in the coupling reaction between styrene and different aryl halides viz
iodobenzene, bromobenzene and chlorobenzene, was checked for five consecutive cycles. It is
clearly visible from fig. 6 that the catalyst maintains its activity in all the cases and gave fairly
good product yields for five consecutive cycles.



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Fig. 6: Catalytic efficiency of Pd-Ni NPs after four consecutive cycles.

The excellent recyclability of the Pd-Ni catalyst was attributed to its chemical stability as demonstrated through leaching experiments. ICP-MS analysis of the reaction mixture showed minimal leaching of active Pd species from catalyst (3.38 ppb). Since there is no significant loss of active species from NPs, the chemical structure and activity is maintained in subsequent cycles. This is affirmed by XRD analysis of NPs recovered after the fourth cycle (Fig. S5, ESI) which does not show any significant change.

In order to further rule out the possibility of catalysis by leached Pd, hot filtration test was performed. In a typical experiment, reaction mixture containing styrene (1 mmol) and iodobenzene (1 mmol) in presence of  $K_2CO_3$  (1.5 mmol) was subjected to MW for 8 mins till the reaction completion after which the hot reaction mixture was filtered to remove any solid catalyst. The filtrate devoid of any solid catalyst (having leached Pd) was charged again with 1

mmol each of styrene and iodobenzene along with K<sub>2</sub>CO<sub>3</sub> (1.5 mmol) and was subjected to MW under similar reaction conditions. The addition of reactants to the system in the absence of Pd-Ni NPs did not show any conversion to the product. We also carried out the reaction in the solvent recovered after complete extraction of the products from the previous batch and no product formation was observed. These results suggest that the achieved catalytic performance is not due to leached Pd but is purely attributed to the presence of Pd-Ni NPs.

# 3.3. Regio and stereoselectivity

The plausible mechanism of the reaction between the reactants on NP surface is general heck type mechanism. The catalytic system facilitates the regioselective intramolecular arylation of electron deficient olefin by different substituted aryl halides (scheme 3) to give exclusive stereoselective product i.e. *trans-* substituted alkenes (verified through the coupling constants data, section S1, ESI). The electronic and stearic factors govern the 2, 1-insertion of olefin (step C, Fig. S6, ESI) resulting in the stereo- and regioselectivity of the products which is in accordance with the literature reports.<sup>50-51</sup> The remarkable catalytic behaviour of the bimetallic system could be attributed to two facts. First, the synergistic effect of two metals, Ni and Pd belonging to the same group. The intermetallic interactions of Ni having higher oxidation potential (+0.25V) with Pd (-0.915V) increase the nucleophilicity at Pd sites of NP that accelerated the oxidative addition. Second, apart from the well-established active Pd(0) sites in NP, Ni(0) sites can also actively add aryl halide oxidizing to Ni(+2) in a similar way in cooperation with Pd sites which is well documented in literature.<sup>52</sup>

### **3.4.** Role of surfactant coating in catalytic activity of NPs

It is noteworthy that surfactant coating on NPs plays a significant role in their catalytic activity in 22 Mizoroki Heck coupling reaction. In order to establish the assertion, the model coupling reaction 23 between styrene and iodobenzene was performed with Pd-Ni NPs without surfactant. The 24 surfactant coating on the NPs was removed by calcination at 150 °C for 2 hours. The IR 25 spectrum of the calcined NPs showed no signal corresponding to dodecylamine affirming that 26 27 the NPs were devoid of surfactant coating (Fig. S7(a), ESI). It was observed that without surfactant coating, the catalytic activity was decreased (60% yield) in comparison to surfactant 28 capped NPs (86% yield). This decrease in catalytic activity on the removal of surfactant coating 29 is attributed to the aggregation of NPs in the absence of surfactant coating which decreases the 30

overall active surface area for the reaction to take place (Fig. S7(b), ESI). It is also noteworthy 1 that removal of surfactant leads to oxidation of Ni present on the surface. The presence of oxide 2 layer (Ni) is evidenced from XRD and EDS patterns of calcined NPs (without surfactant coating 3 (Fig. S7(c) and (d), ESI). Also, the leaching experiments showed comparatively greater loss of 4 active Pd species during the reaction in case of calcined NPs (3.31 ppm) as compared to NPs 5 having surfactant coating (<1 ppm). These observations suggest that the alkyl chains of 6 surfactant, provides chemical stability to NPs apart from ensuring facile diffusion of 7 hydrophobic reactants from water based reaction medium to active metallic sites of NPs. 8

# **3.5.** Comparison of present catalytic system with literature reports

To check the superiority of the present catalytic system, we tested the Mizoroki Heck coupling reaction with different Pd sources that were reported in the literature and also with monometallic Pd and Ni NPs synthesized via same protocol as Pd-Ni alloy NPs. The results have been summarized in Table 2 and it is clearly evident that the present catalytic system is a better approach for Mizoroki Heck coupling in terms of catalyst fabrication, energy-time consumption, environment-friendly and economic aspect as Pd-Ni alloy NPs carrying lesser content of noble Pd element as compared to pure monometallic Pd NPs, performed comparably well.

S. No.	Catalyst	Energy	Solvent	Time	Yield (%	) Reference
		source				
1.	Pd-Ni (1:1) NPs	Conventional heating	DMF	24 hr	82	[43]
2.	Pd-Fe <sub>3</sub> O <sub>4</sub> NPs	Conventional heating	DMF	24 hr	91	[53]
3.	Pd-CuO NPs	Conventional heating	DMF	20 hr	96	[54]
4.	Pd-Mesoporous Organic Polymer	Conventional heating	$H_2O$	6 hr	92	[55]
5.	Pd-ZnO NPs	Conventional heating	H <sub>2</sub> O	17 hr	95	[56]
6.	Pd-Ni (1:1) NPs	Conventional heating	MeOH	18 hr	22	[57]
7.	Pd-Cu (4:1) NPs	Conventional heating	МеОН	18 hr	91	[57]
8.	Pd thin films	MW	DMF	20 min	80	[58]
9.	Pd NPs	MW	Water/EtOH	12 min	86 P	resent work
10.	Ni NPs	MW	Water/EtOH	40 min	76 P	resent work

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11.Pd-Ni (1:1) NPsMWWater/EtOH8 min88Present work

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# 4. Conclusion

In conclusion, a facile solution-based one-pot method has been successfully developed for 5 the synthesis of Pd-Ni alloy NPs ensuring control over growth and size of nanoparticles by using 6 7 metallosurfactants. The as-synthesized NPs have been found to show remarkable catalytic activity in Mizoroki Heck coupling reaction under MW conditions and water-EtOH as the green 8 solvent system. Role of surfactant capping has been established and is found to impart stability to 9 the catalyst to show sustained and enhanced activity over repeated catalytic cycles. Factors such 10 as simple synthetic procedure, wide substrate scope, easy recovery of final products, milder 11 reaction conditions, regio/stereoselectivity, preclusion of toxic reagents advocate for the 12 applicability of present catalytic system in C-C coupling reactions as an efficient, economic and 13 environment-friendly process. The developed protocol for the synthesis of alloy nanoparticles 14 can be further extended in future for the synthesis of various nanoalloys with varied metal ratios, 15 shapes and morphologies to get desired applications viz. hydrogenation reactions, electrocatalysis 16 which are characteristics of metal catalysts. 17

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# **Graphical abstract**

