Tetrahedron 68 (2012) 3001–3011

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Preparation of monometallic (Pd, Ag) and bimetallic (Pd/Ag, Pd/Ni, Pd/Cu) nanoparticles via reversed micelles and their use in the Heck reaction

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ARTICLE INFO

Article history:
Received 27 August 2011
Received in revised form 30 January 2012
Accepted 13 February 2012
Available online 20 February 2012

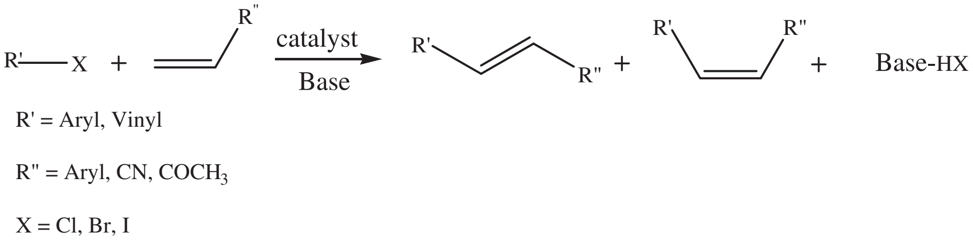
Keywords:
Reverse micelle
Bimetallic nanoparticles
Nano-catalyst
Heck reaction
C–C coupling reaction
Aryl chlorides

ABSTRACT

The metal nanoparticles (NPs) have been prepared using a water-in-oil microemulsion system of water/dioctyl sulfosuccinate sodium salt (aerosol-OT, AOT)/isooctane at 25 °C. Since the NPs produced in this system can endure forcing conditions (100 °C), this system has been used for the synthesis of nano-catalysts in the Heck reactions. FE-SEM, DLS, and UV/vis analyses have been used to characterize the surface morphology, size, and proof of the formation of all the prepared metal NPs, respectively. In addition, the effects of some reaction parameters (here, bases and solvents) were optimized. Differences in the catalytic properties of the synthesized NPs have also been investigated. Consequently, the Pd/Cu (4:1) bimetallic NP showed the highest activity in the C–C coupling reaction of the iodobenzene with the styrene, thus it is employed as the superior catalyst in this study. Therefore, the Pd/Cu (4:1) bimetallic NPs were further investigated using TEM and XRD analyses. This catalyst system is also reusable for six runs with very negligible reduction in the efficiency.

1. Introduction

Due to great progress of nano-catalysts in nano-chemistry and nano-technology, many researchers have recently realized their importance in organic reactions.[1] For example, vinylation of aryl halides, which was discovered by Heck[2] and Mizoroski[3] (Scheme 1) in the early 1970s (commonly called the Heck–Mizoroki reaction), is an important reaction for the synthesis of C–C bond.[4–7] Recently, the commercial and economic aspects to the industrialization of these reactions have been focused on.[8–10] Conventionally, these reactions are carried out in the presence of the palladium catalysts supported by the ligands, such as phosphine, phosphorus, amines, carbene, thiolate etc. However, the ligands, especially phosphine ligands are usually unrecoverable, sensitive to air, expensive, toxic, and degradable at elevated temperatures.[11,12] In addition, these ligands have adverse effects on biological systems.[9] In order to avoid these problems, some researchers have made use of the active catalysts anchored to solid supports.[13,14] In this context, a wide range of organic and inorganic supports including mesoporous silica, zeolites, active carbon, dendronized support have been applied.[15–18] These catalysts are reported to be highly stable and non-destructive; however, some of these supports have a limitation in reusability and thermal stability (which should be also considered as important advantages in the organic reaction).[19–21]



Scheme 1. The Heck–Mizoroki coupling reaction.

Metal NPs are of the highest importance due to their very unique chemical and physical properties.[22] In comparison to the bulk state,

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0040-4020/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2012.02.028

the metal NPs due to their small particle size and high surface-to-volume ratio[23] bring about novel thermal, electronic, optical, magnetic, and chemical properties,[24] and can also cause specific catalytic activities.[25,26] As recorded in the literature, several methods have been developed for metal NPs preparation, including sonochemical methods, citrate reduction, alcohol reduction, laser oblation methods, γ-radiolysis technique, reverse micelle methods etc. Because particle morphology may vary depending on synthesis conditions and since the particles in nano-scale have size-dependent properties.[27] Therefore, it is important to adopt a reliable method for developing uniform and de-agglomerated particles.

The reverse micelle route provides excellent control over the particle size and particle shape of the NPs.[28] Exchanges between the micelles in the solution result in uniform distribution of micelles volume throughout the solution. This makes it possible to control NPs size through controlling micelles diameter. Since all micelles are equal in size, the prepared NPs are fairly homogeneous and uniform.[29,30] Another advantage of this system is that, metal NPs can be synthesized at room temperature, and the surfactants surrounding the particles in the solution can easily be removed.

Since the catalytic activity of transition metals is related to their (d) orbital properties, selecting a suitable metal is the first step for selectivity control and synthesis of the organic reactions.[1] The importance of applying palladium as supported systems of Pd/ligand and Pd/C as a versatile tool in various C–C,[31] C–N,[32] and C–O[33] coupling reactions, including Negishi, Kumada, Suzuki Miyaura, Stille, aryl amination etc., is recognized. However, the yield of the catalysts can change by addition of another element to the metal, thus bimetallic NPs create new properties compared to the monometallic NPs.[34]

For many years, only aryl bromides and iodides were used in Heck reactions. However, the previously used Pd catalysts delayed oxidation–addition step in Pd(II) complexes in aryl chlorides due to the strong C–Cl bond.[10,35] Therefore, efforts have been made to achieve a better catalyst to make the C–Cl bond active. Accordingly, a small number of heterogeneous Pd catalysts have been reported to activate aryl chlorides in difficult conditions.[36–40] In this protocol, we have also developed a novel nano-catalyst anchored to AOT, which can effectively activate C–Cl bond in aryl chlorides.

So far, different methods have been adopted using monometallic NPs to conduct the Heck reaction.[31,41–43] On the other hand, application of bimetallic NPs prepared by microemulsion has not yet been properly investigated in most organic reactions. In this paper, our purpose is to design an effective catalytic system in which the Heck reaction is conducted by using bimetallic NPs. Then, the reaction conditions are optimized and the results are evaluated.

2. Results and discussion

2.1. Analysis of catalyst NPs

Metal NPs color change is very evident after the addition of the reducing agent, which implies that the metal NPs are reduced. For instance, the brown color of the Pd/Cu (4:1) changed immediately into black after the addition of hydrazine hydrate. All the samples changed into dark brown or black after reduction. These color changes before and after reduction process are shown in Fig. 1.

The preparation conditions affect the structure, shape, and size distribution of the metal NPs. Therefore, due to the said reasons (as stated in the introduction); the reverse micellar method is one of the most preferred candidates. The first question relating to the metal NPs is to investigate the aggregation state, size, and morphology. The surface morphology of all the synthesized samples was investigated by FE-SEM, as shown in Fig. 2. The FE-SEM images indicate that the synthesized NPs are approximately uniform and spherical in shape.

Fig. 1. Digital photographs of microemulsions before (the upper) and after (the lower) reduction with hydrazine hydrate. (a) Pd; (b) Ag; (c) Pd/Ag (1:1); (d) Pd/Ni (1:1); (e) Pd/Cu (4:1).

DLS analysis was used to characterize the particle size distribution. Fig. 3 shows the particle size distribution of Pd, Ag, and Pd/M NPs, obtained from of DLS analysis, and Fig. 4 shows the UV/vis absorption spectra of these mono- and bimetallic metal NPs. DLS data have shown a narrow particle size distribution. Both the UV/vis absorption spectra and DLS analysis indicate the formation of metallic NPs.

UV/vis spectrometry was chosen to prove the formation of metal NPs because of its reliability and feasibility. Reducing the metal ions causes a decrease in the plasmon band intensity and a flattening of the peak. As shown in Fig. 4, absorption peaks are flattened after the addition of reducing agent indicating that the metal ions vanish. In addition, blue shift after the addition of reducing agent supports the formation of NPs.

For Pd NPs before and after reduction (synthesized by the same method), similar spectra have already been reported in the literature.[44] The absence of Pd plasmon band (λ_{max}=420 nm) in the Pd/M (M=Ag, Ni, and Cu) bimetallic NPs indicates that only bimetallic NPs are formed. If bimetallic NPs were not formed, two adsorption peaks would be observed in UV/vis spectra for each metal. It has been proved in advance that physical mixtures of the two NPs have two individual spectra.[45] Appearance of only one absorption band indicates the formation of bimetallic NPs. On the other hand, existence of Pd metal in bimetallic NPs usually suppresses the surface absorption plasmon,[46–49] which is more obvious for Pd/Ni and Pd/Cu in our work. Also, it has been proved that bimetallic NPs bring about some changes in the surface plasmon band.[50,51] These observations are compatible with Mie theory,[52] first reported in 1908. According to this theory, when a metal is of nanometer dimensions (in contrast with the bulk state), a size-dependent blue shift in the photoelectron band (i.e., hypsochromic effect) occurs. Such a behavior of small particles is due to the size-dependent distribution of the electron energy levels (quantum-size effect). In other words, normal position of plasmon band shifts toward a shorter

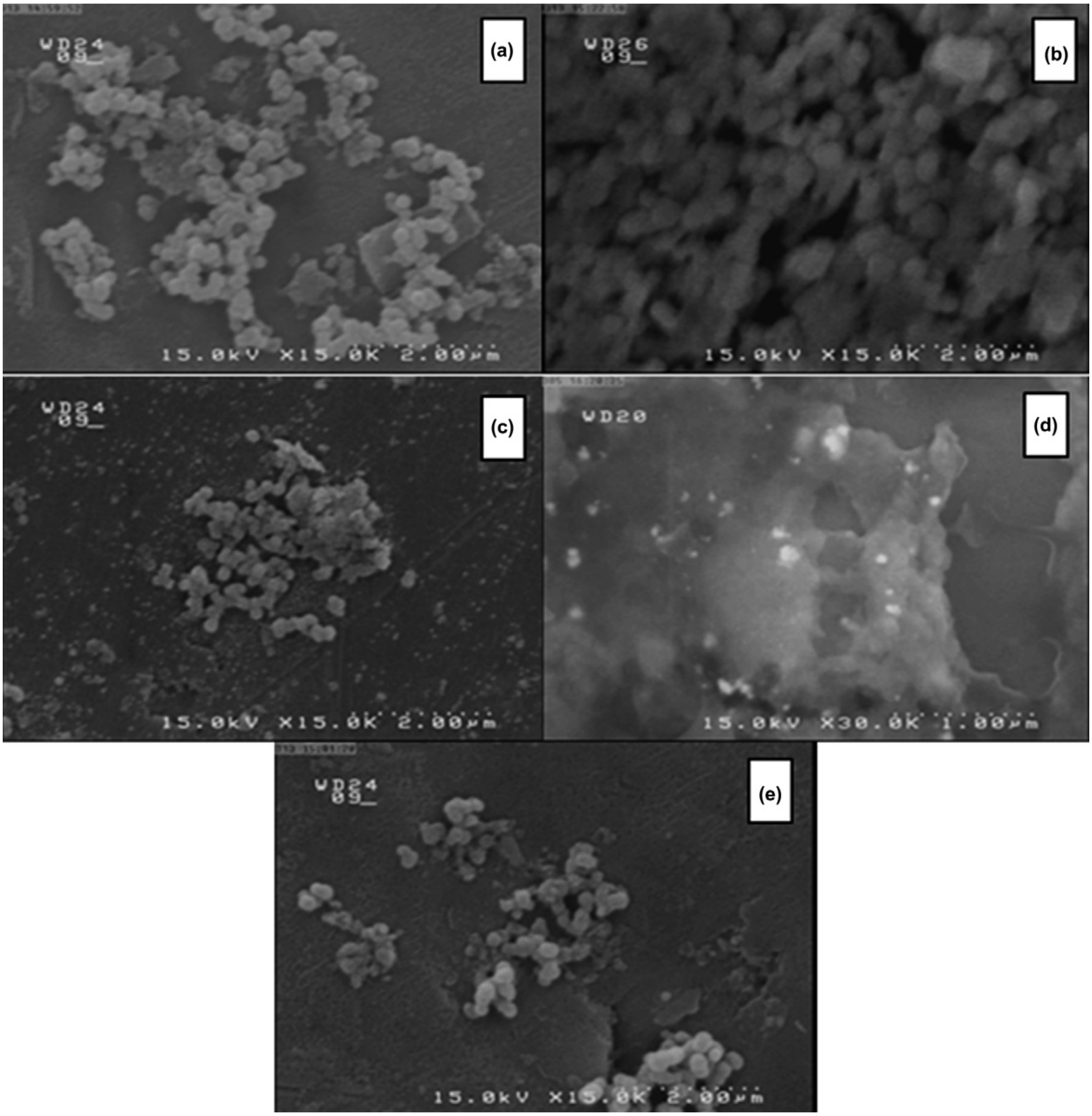


Fig. 2. FE-SEM images of (a) Pd, (b) Ag, (c) Pd/Ag (1:1), (d) Pd/Ni (1:1), (e) Pd/Cu (4:1).

wavelength with a decrease in the particle size. These effects can be explained by the fact that absorption band is closely dependent on the particle size. Also, with the more reduction of the metal ions, the absorption band is broadened (due to the d–d interband transitions) and then vanished.

In Fig. 4(a), the absorption spectrum of the micelle solution without metal salt is shown. According to this figure, the absorption band (λ_{max}=234 nm) is related to the presence of the surfactant molecules, which is broadened after reducing agent is added to the solution. However, this is out of the scope of the present study and will be discarded.

For further investigation of the Pd/Cu (4:1) bimetallic NPs (as the superior catalyst in this study), the structure and size of the considered NPs were characterized using XRD and TEM analyses. Among the most frequently used techniques, TEM analysis is indispensable for the metal NPs studies. For TEM analysis, the synthesized sample was prepared by placing a drop of microemulsion solution onto the carbon coated copper TEM grids and drying it in air at room temperature. In Fig. 5, the TEM image of the Pd/Cu (4:1) bimetallic NPs shows the existence of uniform, mono-disperse, and spherical particles.

X-ray diffraction is an effective method for investigation of the solid structure of NPs. Therefore, the particle structure of the Pd/Cu (4:1) NPs was further characterized by the XRD analysis. In order to prepare the catalyst sample for XRD analysis, methanol was first added to the reverse micellar solutions for phase separation, then the mixture was centrifuged, and the catalyst was washed with methanol three times, and finally the obtained catalyst was dried at room temperature. Fig. 6 shows the phase composition of Pd/Cu (4:1) catalyst by the XRD analysis. The phase was identified by comparison with the Joint Committee on Powder Diffraction Standards (JCPDSs). Because of the different peak positions of Pd, Cu, and Pd/Cu NPs in the XRD pattern, it is very effective to employ the XRD analysis for the determination of the Pd/Cu (4:1) NPs structure. The characteristic peaks for Pd (JCPDS number of card, 05-0681; 2θ=40°, 46.7°, 68°, 82°, and 86.0°) and those for Cu (JCPDS number of card, 85-1326; 2θ=43.3°, 50.5°, 74.2°, and 89°), marked by their indices ((111), (200), (220), (311), (222)),

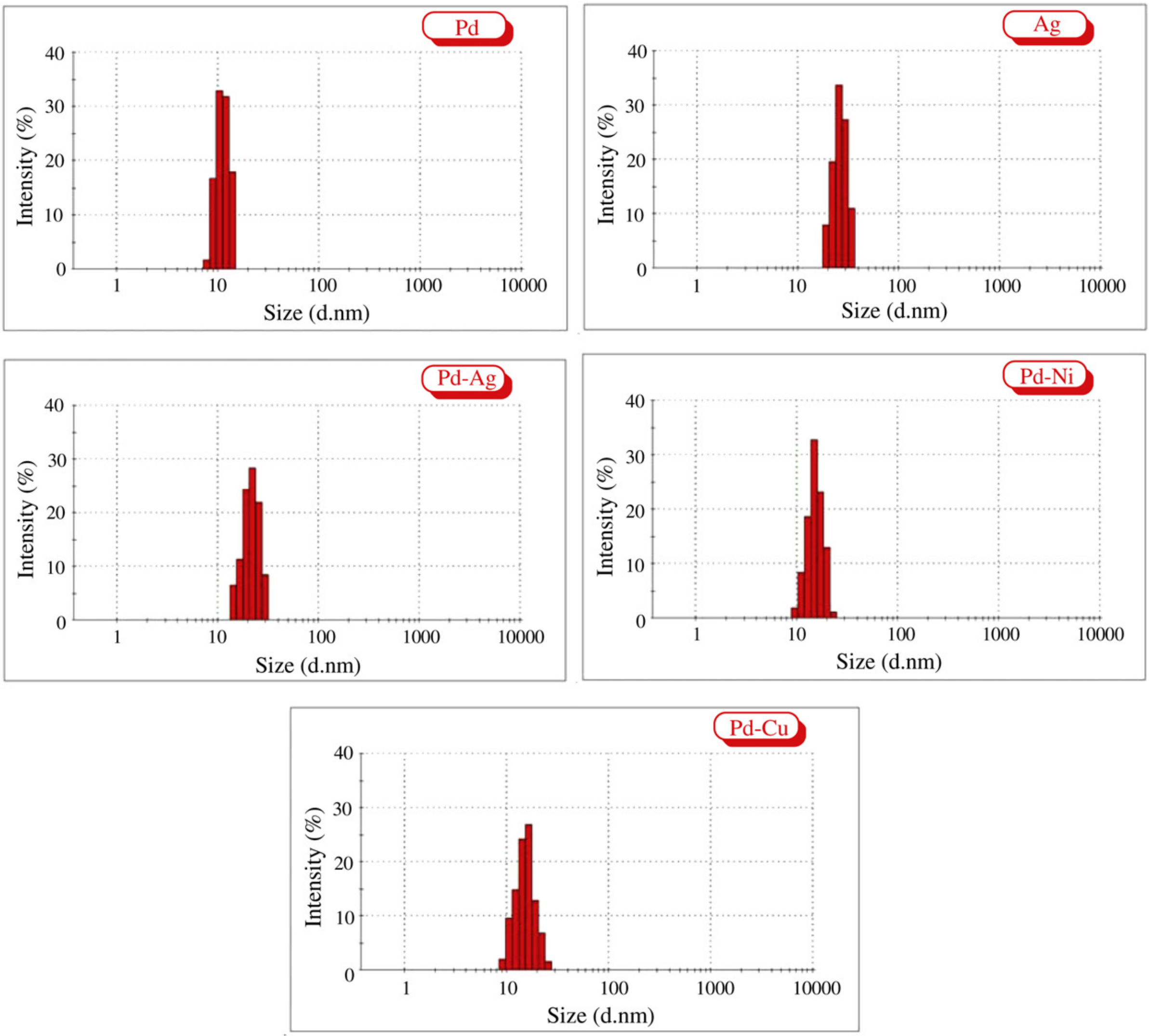


Fig. 3. Particle size distribution of mono- and bimetallic NPs by DLS analysis.

demonstrate the presence of the face-centered cubic (fcc) Pd and Cu crystallite planes. The XRD pattern of the Pd/Cu (4:1) catalyst in Fig. 6 appears at 2θ values of 40.32°, 47.18°, 68.28°, 82.34°, and 86.12° corresponding to the planes (111), (200), (220), (311), and (222) with fcc structure. In this XRD pattern, the five characteristic diffraction peaks are corresponding to the planes of Pd, but the presence of copper could affect the diffraction angles of Pd (shift to higher 2θ values) as a result of copper incorporation into the Pd particle or alloy formation. To give an example, despite the fact that the 2θ value of diffraction peak of Pd for the plane (111) was located at 40°, the 2θ value of diffraction peak of the Pd/Cu (4:1) catalyst in the plane (111) in our XRD pattern is located at 40.32°, demonstrating that the formation of single-phase alloy causes the 2θ value to shift upward by $\Delta 0.32°$. In other words, this issue indicates that a portion of Cu has entered the Pd lattice, forming the Pd/Cu alloy phase. Also, since the radius of the Cu metal is smaller than that of the Pd, the 2θ values of the diffraction peaks of the Pd/Cu alloy are larger than those of the Pd particles, which follows the Vegard's law.[53] The XRD pattern of Pd/Cu (4:1) showed that no characteristic peak of Cu existed, which can be attributed to the low content of the Cu in the Pd/Cu (4:1) bimetallic NP. Also, no characteristic peaks for cuprous oxides ($Cu(OH)_2$, Cu_2O or CuO) were observed. Despite the presence of dissolved oxygen in the solvent, the diffraction peaks of oxides phase (i.e., $2\theta=34°$, 36.5°, 42.58°, and 61.4°) were not detected, showing that the Cu NPs were very stable against further oxidation.

Using the Debye–Scherrer equation, the average particle size (t) of the Pd/Cu (4:1) NPs is calculated to be 15 nm as follows (Eq. 1).

$$t = k\lambda/\beta\cos\ \theta \qquad (1)$$

Due to the small particle size of the NPs, the peaks observed in the XRD pattern are relatively broad. The calculated size matches approximately to the size observed from TEM image and DLS analysis. In this equation, t is the average particle size, k is the so-called shape factor, which usually takes a value of about 0.9, λ is the wavelength of the incident radiation, β is the full width in radians at half-maximum intensity (FWHM), and θ is the angle at maximum diffraction curve intensity.

All the analyses have consistently shown fairly uniform NPs with small size. Recent literature has shown that synthesizing uniform NPs for organic reactions has attracted much attention.

2.2. Optimization of the reaction conditions

2.2.1. Catalytic testing. Initially, the Heck reaction of iodobenzene and styrene was chosen as a model reaction. Loading of the catalyst, bases, and solvents were screened to optimize reaction conditions.

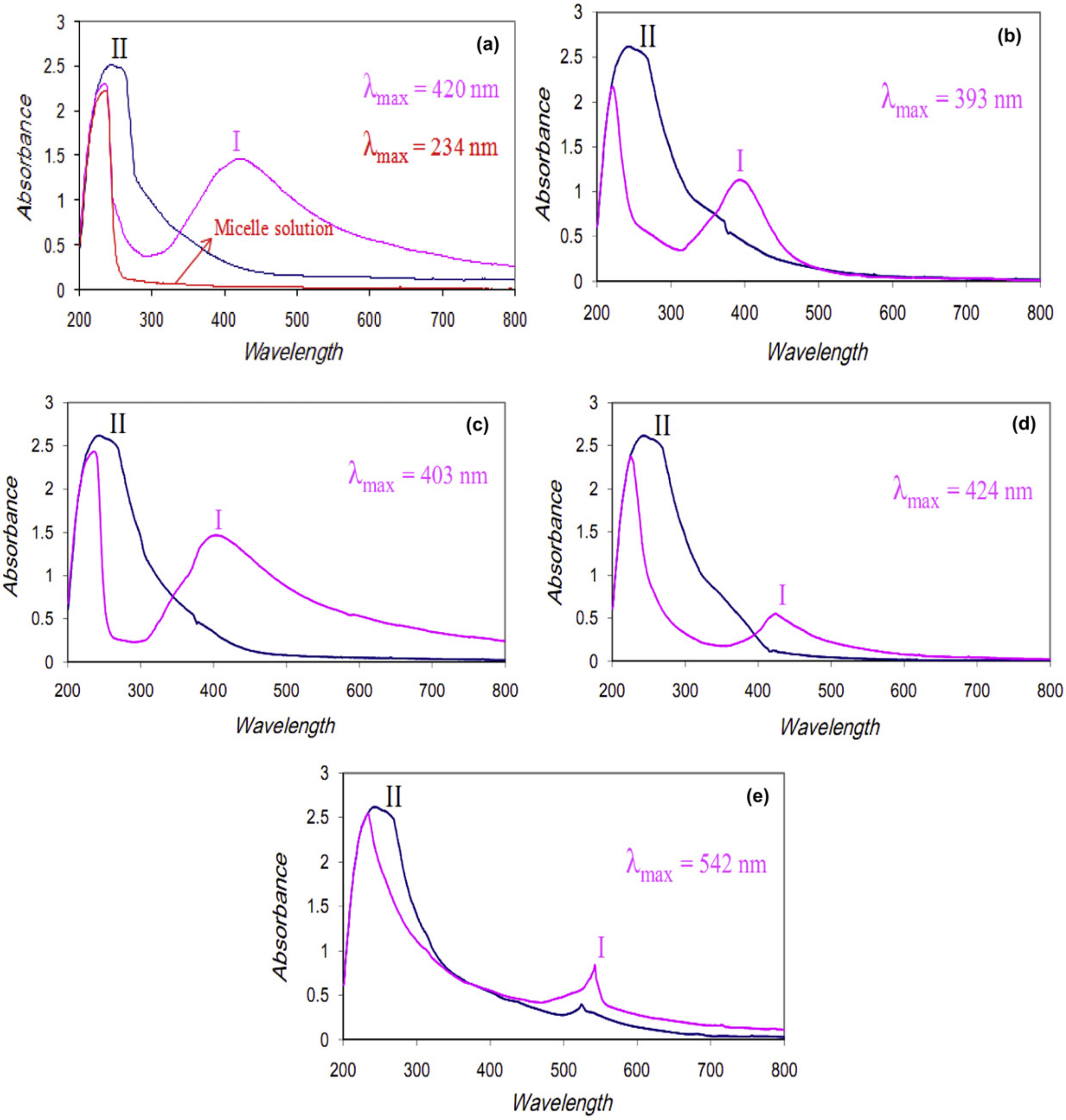


Fig. 4. Typical UV/vis spectra of microemulsions before (I) and after (II) reduction with hydrazine hydrate. (a) Pd; (b) Ag; (c) Pd/Ag (1:1); (d) Pd/Ni (1:1); (e) Pd/Cu (4:1).

Since most papers in the literature indicate that the use of the metals, such as Pd, Cu, and Ni in different systems can activate the C–X bond (X=Cl, Br, and I) in the coupling reactions, we have investigated these metals as bimetallic NPs in our system. For practical application in the Heck reaction, the lifetime, thermal stability and reusability of prepared catalysts are very important factors.

A number of catalyst sources were examined in optimization experiments. The rate and activity of the prepared catalysts in the Heck reaction are compared and listed in Table 1. It should be noted the turn over numbers (TONs) and the turn over frequencies (TOFs), which are defined as mmol product/mmol catalyst and mmol product/mmol catalyst per hour, were calculated from the isolated yield. The reaction with no catalyst yielded only a small amount of product (entry 1). When metal salts were used, results were not acceptable (entries 2 and 3) as palladium(II) sources did not show significant catalytic activity. Application of silver NPs showed that the silver can decrease the Pd NPs activity in this reaction (entries 4–6). When a ratio of 1:1 of the bimetallic NPs was applied (entries 6–8), Pd/Cu showed the highest product yield. Therefore, different ratios of this catalyst were investigated (entries 9–11). The highest catalytic activity was achieved by Pd/Cu (4:1) bimetallic NP (entry 10). When this ratio changed to 5:1, the reaction yield decreased (entry 11). As a result, the catalytic efficiency decreases in the order of Pd/Cu (4:1)>Pd>>Pd/Ni (1:1)>Pd/Ag (1:1)>Ag. (For the sake of simplicity, only the 4:1 ratio is here mentioned for Pd/Cu as the best catalyst in the said order). All of the achieved products were trans-isomers, which were identified by GC.

In practical use, developing catalysts that keep their catalytic activity for a prolonged time is a major problem. In the present work, we have studied the potential recycling process of Pd (as a common metal in the Heck reaction) and Pd/Cu (4:1) (as the superior catalyst in this study) catalysts. The catalytic stability of these two catalysts up to seven runs at 100 °C (in the Heck reaction of the iodobenzene with the styrene) is shown in Fig. 7. Before the next run, the catalyst system was easily separable—by centrifugation—from the reaction mixture by decantation of the liquid

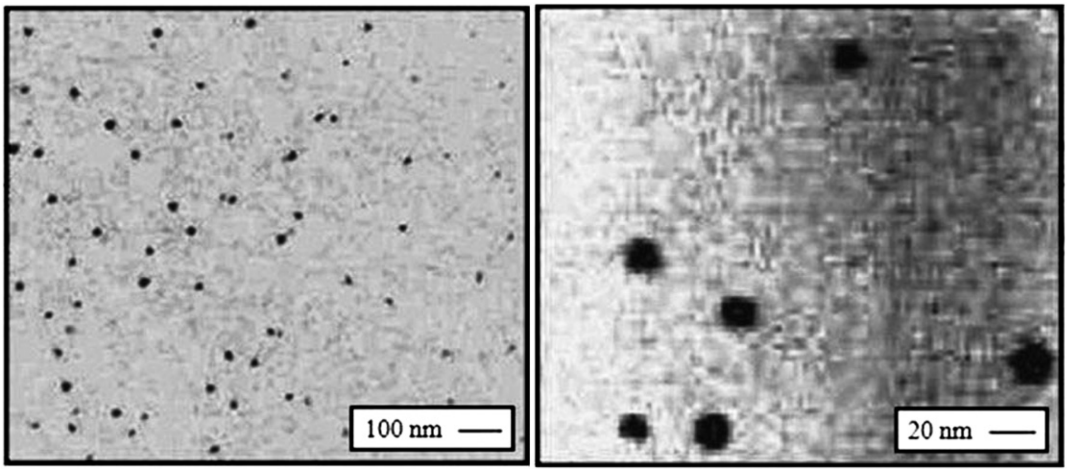


Fig. 5. TEM image of spherical Pd/Cu (4:1) bimetallic NPs formed in the microemulsion.

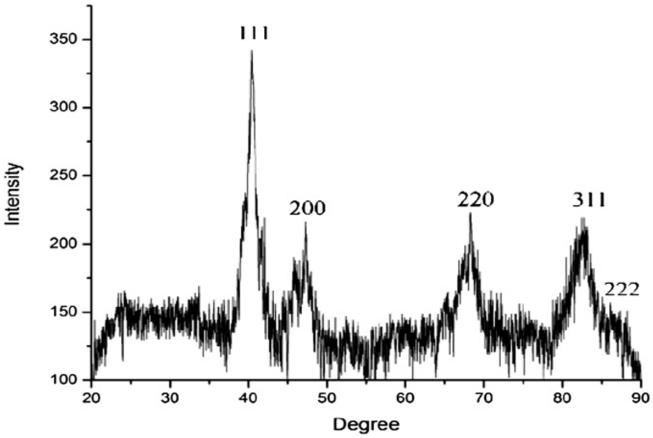


Fig. 6. X-ray diffraction (XRD) spectrum of Pd/Cu (4:1) bimetallic NPs synthesized in water/AOT/isooctane reverse micelles.

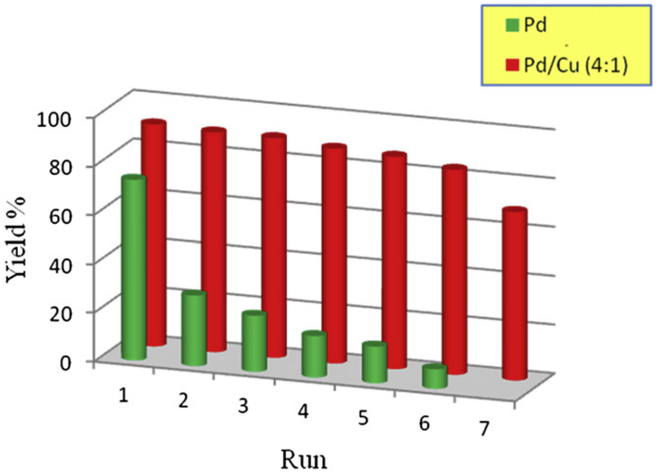


Fig. 7. Comparison of yield and reusability of Pd and Pd/Cu (4:1) NPs as catalysts in the Heck reaction of the iodobenzene with the styrene at 100 °C.

Table 1
The effect of different catalysts on the reaction of iodobenzene and styrene[a]

Entry	Catalyst	Yield[b] (%)	TON[c]	TOF[c] (h^{-1})
1	None	Trace	—	—
2	$PdCl_2$	11	713	40
3	Pd $(OAC)_2$	14	907	50
4	Pd	74[d]	4806	267
5	Ag	Trace	—	—
6	Pd/Ag (1:1)	7	455	25
7	Pd/Ni (1:1)	22	1424	79
8	Pd/Cu (1:1)	49[d]	3187	177
9	Pd/Cu (2:1)	56[d]	3642	202
10	Pd/Cu (4:1)	91[d]	5921	329
11	Pd/Cu (5:1)	82[d]	5335	296

[a] Reaction condition: iodobenzene (2 mmol), styrene (3 mmol), NEt_3 (4 mmol), catalyst (4.5×10^{-4} mmol), MeOH (4 mL), 100 °C, 18 h.

[b] Yield was determined by GC, which was then compared to an internal standard.

[c] Calculated from the isolated yields.

[d] Yields are an average of two runs.

phase, and then the catalyst was washed with diethyl ether, dried at 60 °C, and was used for a new run. Each reaction was run for 18 h, which was the necessary time for completing the reaction. In case of Pd catalyst, when this treatment was performed, a significant decrease in the catalytic activity of Pd NPs was observed after each run, so that by the second run, the activity decreased with a yield of 74–29%. Then, the catalytic activity decreased gradually so that in the sixth run the yield was 8% (TON=514, TOF=28.5 h^{-1}). These results can be attributed to the decreasing amount of Pd catalyst versus the number of cycles, which in turn show that the contribution of Pd catalyst in the C–C coupling reaction of the iodobenzene with the styrene is important. On the other hand, the feature of the Heck reaction with Pd/Cu (4:1) is different so that almost no loss of catalytic activity was observed after six runs. However, after the sixth run, more decrease in the efficiency was observed, compared to the previous runs (TON=4491, TOF=249.5 h^{-1}), i.e., a 22% decrease compared with the first run. These results show that the amount of leached catalyst after each run is low. In general, this catalyst (Pd/Cu (4:1)) is easily separable and recyclable in six successive runs with little reduction in catalytic efficiency.

2.2.2. Effect of the base. Bases perform an essential role in the Heck reaction since they can accelerate and regenerate catalysts. In order to regenerate catalyst for Heck reaction, base is required to neutralize and remove HX from H–Cat–X intermediate. In the process of coupling reaction, it is important to select a base and solvent, so these parameters were optimized and the experimental results are presented in Tables 2 and 3, respectively. The reaction without catalyst or base afforded no product (entry 1).

Based on the type of catalytic system applied, bases show different effects on Heck reaction.[54] In view of that, previous

Table 2
The effect of different bases on the reaction of iodobenzene and styrene[a]

Entry	Base	Yield[b] (%)	TON[c]	TOF[c] (h^{-1})
1	None	Trace	—	—
2	NEt_3	91[d]	5921	329
3	K_2CO_3	75[d]	4879	271
4	KOAC	19	1235	69
5	Na_2CO_3	35	2274	126
6	NaOH	11	713	40
7	$CsCO_3$	31	2012	112
8	$NaPO_4$	40	2605	145

[a] Reaction condition: iodobenzene (2 mmol), styrene (3 mmol), base (4 mmol), Pd/Cu (4:1) (4.5×10^{-4} mmol), MeOH (4 mL), 100 °C, 18 h.
[b] Yield was determined by GC, which was then compared to an internal standard.
[c] Calculated from the isolated yields.
[d] Yields are an average of two runs.

Table 3
The effect of different solvents on the reaction of iodobenzene and styrene[a]

Entry	Solvent	Yield[b] (%)	TON[c]	TOF[c] (h^{-1})
1	DMF	100	6510	362
2	CH_3CN	13	842	47
3	THF	27	1754	97
4	*n*-Hexane	N.R	—	—
5	DMSO	17	1106	61
6	MeOH	91[d]	5921	329
7	Toluene	42	2733	152

[a] Reaction condition: iodobenzene (2 mmol), styrene (3 mmol), NEt_3 (4 mmol), Pd/Cu (4:1) (4.5×10^{-4} mmol), solvent (4 mL), 100 °C, 18 h.
[b] Yield was determined by GC, which was then compared to an internal standard.
[c] Calculated from the isolated yields.
[d] Yields are an average of two runs.

reports have mentioned $NaHCO_3$,[9] K_3PO_4,[43] and KOAc[55] as the best bases. In Table 2, entries 2–8, effects of different bases on the Heck reaction are compared. The highest yield and selectivity were observed in the presence of K_2CO_3 and NEt_3 (entries 2 and 3). On the contrary, low yields were achieved when NaOH was used (entry 6).

NEt_3 has previously been reported as a base with low product yield;[56–58] this may be due in part to blocking of free coordination sites on the palladium center by ligands, dendrimers, organic and inorganic supports. However, in our study, the applied NEt_3 has given a desired effect, which is thought to be due to the existence of free coordination site at the catalyst center. Because of the great importance attached to the bases, it is required that they should be further investigated in the future.

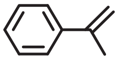
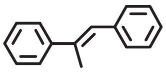
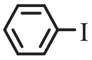
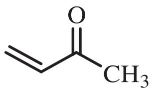
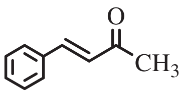
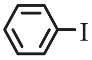
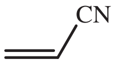
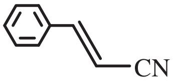
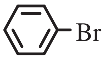
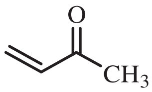
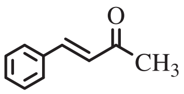
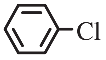
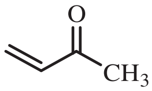
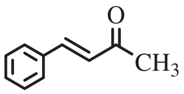
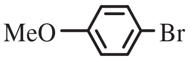
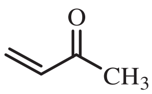
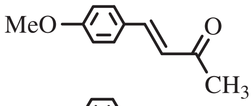
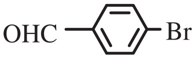
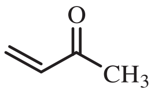
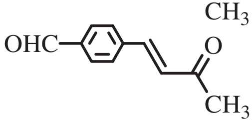
2.2.3. Effect of the solvent. Several organic solvents, such as DMF, CH_3CN, THF, *n*-hexane, DMSO, MeOH, and toluene were examined. The experimental results are summarized in Table 3. Similar to bases, the solvents can also cause different effects on the Heck reaction, depending on the used catalyst system.[59,60] In our system, DMF was found to be more effective than other solvents (entry 1), which was consistent with some of the previous reports. Solvents like CH_3CN and DMSO did not produce a good yield possibly due to their high coordination ability (entries 2 and 5). The lowest efficiency resulted when non-polar *n*-hexane solvent was applied (entry 4).

Both our study and previous reports have indicated that aprotic polar solvents give a good performance. Therefore, the best system for this reaction was DMF in combination with NEt_3, and Pd/Cu (4:1) bimetallic NP as catalyst.

2.3. Heck cross-coupling reactions

Using the optimized reaction conditions, a broad sampling of functionalized substrates was employed with good to excellent yields. A range of substituents including OMe, CHO, $COCH_3$, NO_2, NH_2, COOH, OH, CN, I, Br, and Cl were compatible with this procedure. The results are listed in Table 4, entries 1–18. We found that the yields of the C–C couplings were in the range of 66–100%,

Table 4
Heck reaction of aryl halides with olefins catalyzed by Pd/Cu (4:1)[a]

Entry	Aryl halide	Olefin	Product	Yield[b] (%)	TON[c]	TOF[c] (h^{-1})
1				94	6291	349.5
2				100	5919	329
3				93	5185	288
4				88	6401	355.5
5[e]				66[d]	5867	245.5
6				77	5859	325.5
7				96	7497	416.5

(continued on next page)

Table 4 (*continued*)

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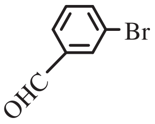
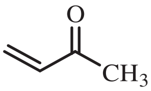
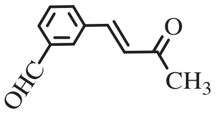
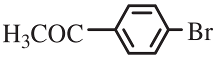
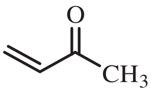
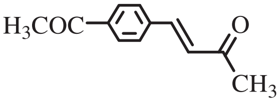
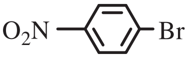
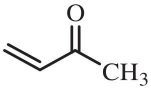
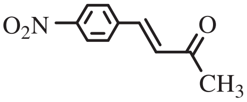
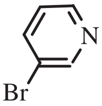
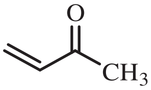
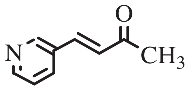
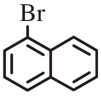
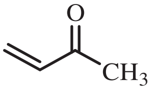
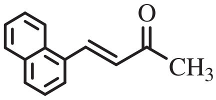
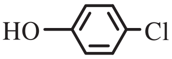
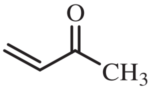
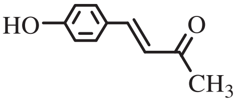
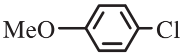
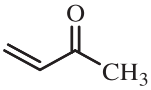
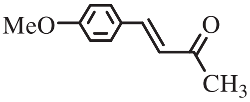
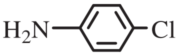
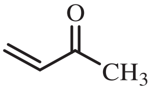
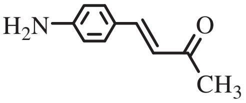
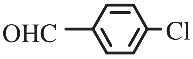
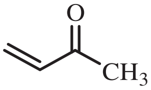
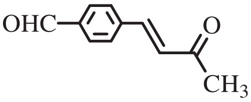
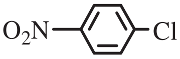
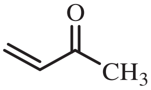
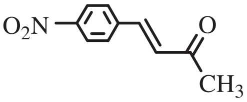
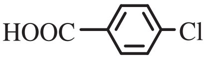
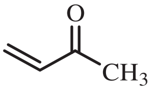
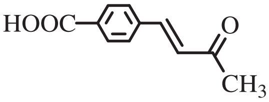
8				91	6906	383.5
9				94	7293	405
10				97	7570	420.5
11				74	5445	302.5
12				90	7077	393
13[e]				77[d]	6978	291
14[e]				73[d]	6717	280
15[e]				78[d]	7064	294
16[e]				85[d]	7834	326.5
17[e]				79[d]	7165	298.5
18[e]				84[d]	7822	326

[a] Reaction condition: aryl halides (2 mmol), olefin (3 mmol), NEt_3 (4 mmol), Pd/Cu (4:1) (4.5×10^{-4} mmol), DMF (4 mL), 100 °C, 18 h.

[b] All compounds are characterized by comparison of GC analysis.

[c] Calculated from the isolated yields.

[d] Yields are an average of two runs.

[e] At 120 °C for 24 h.

corresponding to the TONs from 5867 to 5919. This catalyst system has relatively higher TONs and TOFs than some other systems. The structures of the products were deduced according to the physical properties and spectroscopic data.

The nature of the olefin exerts a significant effect on the yield and selectivity of the reaction. The Heck reaction of various olefins with iodobenzene proceeded easily at 100 °C resulting in corresponding coupling products in excellent yields after 18 h (entries 1–3). It is usually difficult to activate aryl halides because the C–X bond (X=I, Br, and Cl) has a relatively high bond energy. When the C–C coupling reaction changed from iodine to chlorine, the yield decreased because of the reaction sensitivity to the nature of halogen (entries 2, 4, and 5). It is clear that the reaction of chlorobenzene with olefins took about 24 h for completion. As indicated in the table, the coupling reactions of aryl chlorides with methyl vinyl ketone required higher temperatures and extended reaction times because the oxidative-addition of C–Cl bond to catalyst species is usually difficult. The reaction of aryl halides with electron-withdrawing in the *para* and *meta* positions proceeded smoothly (entries 7–10 and 16–18), while aryl halides with electron-donating substituents were less reactive (entries 6 and 13–15). It would seem that presence of strong electron-withdrawing groups on the aryl halide makes it more susceptible to further oxidative-addition to the catalyst species. The trans-isomer was formed as the dominant coupling product in all cases. As a good advantage of the presented catalyst by this method, product was obtained with excellent yield and complete conversion (100%).

We suggest that the presence of copper in Pd/Cu bimetallic NPs results in the facilitation of electron transfer in the cycle. In general, according to the recent studies, the addition of the second metal to the catalytic system can improve the activity, selectivity, and stability of catalysts in the organic reactions.

3. Conclusion

In conclusion, a simple method for preparing spherical metal NPs (Pd, Ag, Pd/Ag, Pd/Ni, and Pd/Cu) has been adopted based on the reverse micelle technique. The FE-SEM, UV/vis, and DLS analyses all have indicated the formation of NPs. In the C–C coupling process, the catalytic activities of these mono- and bimetallic NPs have been compared. The catalytic efficiency in the Heck reaction has decreased in the order of Pd/Cu (4:1)>Pd>>Pd/Ni (1:1)>Pd/Ag (1:1)>Ag. Bases and solvents have been screened to optimize the reaction conditions. The Pd/Cu (4:1) bimetallic NP proves to be the superior catalyst with high activity and excellent selectivity for the Heck reaction of aryl halides with alkenes. Thus, in order to determine the phase composition, structure, and more accurate size of Pd/Cu (4:1) bimetallic NPs as the best catalyst have been further investigated using TEM and XRD analyses—in addition to FE-SEM, UV/vis, and DLS analyses. This catalyst was simply recovered and recycled for further reactions up to six runs with a negligible loss of efficiency. In our experiments, the aryl chloride has been successfully activated using the presented catalyst. This catalyst is non-toxic, reusable, thermally stable, and makes it possible for the reactions to occur in air. The trans-isomer was formed as the dominant coupling product in all cases. The present study is the first report in which the Pd/Cu (4:1) bimetallic NP, developed in the reverse micelle system, is exploited as an excellent catalyst in the Heck reaction.

4. Experimental

4.1. Materials

The following chemicals were used in the synthesis procedure: palladium(II) acetate ($Pd(OAc)_2$ ≥99%, Merck), nickel(II) acetate tetrahydrate ($Ni(OAc)_2 \cdot 4H_2O$ 98%, Aldrich), copper(II) acetate monohydrate ($Cu(OAc)_2 \cdot H_2O$ ≥99%, Merck), palladium(II) chloride ($PdCl_2$ ≥59%, Merck), silver nitrate ($AgNO_3$ 99.8%, Merck) as precursor salts; dioctyl sulfosuccinate sodium salt (aerosol-OT, AOT 98%, Aldrich) as a surfactant; hydrazine hydrate ($N_2H_4 \cdot H_2O$ ≥99%, Merck) as a reducing agent; isooctane (≥99%, Merck) as the oil phase; methanol (≥99.9%, Merck) as a washing agent and solvent; and water used in the experiments was deionized (DI) and doubly distilled prior to use as the aqueous phase in reverse micelle system. Substrates were purchased from Merck Company, and were used without further purification or drying.

4.2. Characterization

The size, phase composition, shape or morphology of the Pd/Cu (4:1) bimetallic NPs were characterized by dynamic light scattering (DLS), field emission scanning electron microscope (FE-SEM), X-ray diffraction (XRD), transmission electron microscopy (TEM) analyses, and UV/vis spectra. Also, other synthesized mono- and bimetallic NPs (Pd, Ag, Pd/Ag (1:1), Pd/Ni (1:1)) were characterized just by the FE-SEM, DLS analyses, and UV/vis spectra. FE-SEM images were obtained on a Hitachi S-1460 field emission scanning electron microscope using accelerating voltage of 15 kV. The particle size distribution was measured using Brookhaven 90 Plus, DLS spectrometer. The UV/vis spectra of the reverse micelle solutions containing various NPs were measured in a quartz cell using a Camspec M330 UV/vis spectrometer (200–800 nm). TEM measurement for Pd/Cu (4:1) NPs was performed on a Philips model EM 208S instrument operated at an accelerating voltage of 100 kV. XRD analysis of the Pd/Cu (4:1) NPs was carried out using a Philips diffractometer (Model TW 1800). Nickel filtered Cu Kα radiation source was used to produce X-ray (λ=1.542 Å), and scattered radiation was measured with a proportional counter detector at a scan rate of 4°/min. The scanning angle was from 20° to 90°, operating at a voltage of 40 kV applying potential current of 30 mA. Gas Chromatography (GC) data was recorded on a GC Shimadzu 14B with a CBP5 column (25 m×0.25 mm×0.25 μm).

4.3. Preparation of the catalyst

4.3.1. Preparation of the Pd and Ag monometallic NPs. In two separate 25 mL beakers, two microemulsions with different aqueous phases, one with 0.036 mmol $Pd(OAc)_2$ (or 0.03 mmol $AgNO_3$) and the other one with 0.8 mmol $N_2H_4 \cdot H_2O$ were prepared (note that each microemulsion was formed with 0.1 M AOT concentration and a given amount of isooctane as oil phase). Then, the microemulsion containing an aqueous solution of hydrazine hydride was added to the microemulsion containing an aqueous solution of $Pd(OAc)_2$ or $AgNO_3$. Obviously, the solution became dark brown immediately after mixing. The corresponding reduction reactions can be expressed as (Eqs. 2 and 3):

$$2Pd^{2+} + N_2H_5^+ + 5OH^- \rightarrow 2Pd^0 + N_2 + 5H_2O \qquad (2)$$

$$4Ag^+ + N_2H_5^+ + 5OH^- \rightarrow 4Ag^0 + N_2 + 5H_2O \qquad (3)$$

The reaction was allowed to proceed with stirring for 40 min. Then, methanol was added to the beaker to make phase separation and to wash the solution. The final mixture was centrifuged to get samples. Finally, the synthesized NPs were characterized by FE-SEM, DLS analyses, and UV/vis spectra.

4.3.2. Preparation of the Pd/M (M=Ag, Ni, and Cu) bimetallic NPs. Fig. 8 illustrates the general sketch for the preparation process of bimetallic NPs highly dispersed using the reverse micelle method.[61] This general sketch has been applied in our study to synthesize the Pd/Cu (1:1) bimetallic NP as follows. Three microemulsions with different aqueous phases containing 0.018 mmol $Pd(OAc)_2$ (as microemulsion A), 0.018 mmol $Cu(OAc)_2 \cdot H_2O$ (as microemulsion B), and 0.8 mmol $N_2H_4 \cdot H_2O$ (as microemulsion C) were prepared. Then, microemulsion A was mixed to microemulsion B; hereafter the resultant microemulsion is called system I. After mechanical agitation for about 15 min, microemulsion C was added to system I. The corresponding reduction reactions can be expressed as (Eq. 4):

$$2Pd^{2+} + N_2H_5^+ + 5OH^- \rightarrow 2Pd^0 + N_2 + 5H_2O \qquad (4)$$

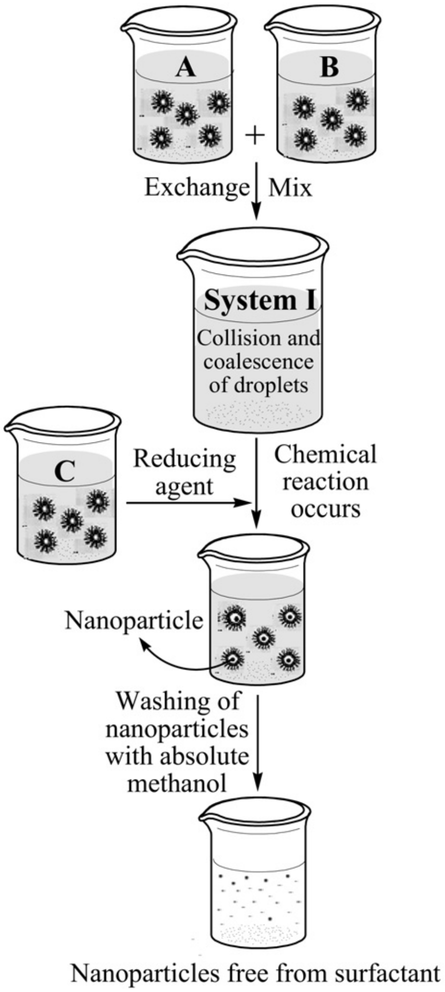


Fig. 8. General sketch for the preparation process of bimetallic NPs.

$$2Cu^{2+} + N_2H_5^+ + 5OH^- \rightarrow 2Cu^0 + N_2 + 5H_2O$$

This bimetallic NP was immediately black in color after 1 min from the addition of the hydrazine hydrate solution (as reducing agent). But in order to complete the reduction of the metal ions, the reaction time was held for 40 min with rapidly stirring at room temperature. After that, the considered NP was separated by centrifuging and was washed with methanol for 5 min three times. Finally, the catalyst (the obtained NP) was dried at 60 °C. This NP (Pd/Cu) was physically characterized by FE-SEM, DLS, UV/vis, TEM and XRD analyses. Other bimetallic NPs (Pd/Ag and Pd/Ni) were synthesized in a similar manner.

4.4. General procedure of the Heck coupling reactions of iodobenzene with styrene

In a 100 mL two-necked flask, the mixture of iodobenzene (2 mmol), styrene (3 mmol), NEt_3 (4 mmol), and the nano-catalyst solution (4.5×10^{-4} mmol) were added in methanol (4 mL). The flask was sealed and the mixture was allowed to stir in a preheated oil bath at 100 °C for the appropriate time. The reactions were monitored by thin layer chromatography (TLC). After the reaction was completed, the reaction mixture was then cooled at room temperature. The solid nano-catalyst was separated by centrifuge and washed with water to remove base and salt. The remaining solution was then washed with acetone to remove adsorbed organic substrate. Finally, the prepared samples were analyzed by GC.

Acknowledgements

We would like to thank K.N. Toosi University of Technology research council for financial support.

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