Heterogeneous Catalysis



Nano PdAu Bimetallic Alloy as an Effective Catalyst for the Buchwald–Hartwig Reaction

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Abstract: It is highly challenging but desirable to develop efficient heterogeneous catalysts for C–Cl bond activation in coupling reactions. Here, we succeeded in synthesizing bimetallic Pd-Au nanoparticles through a convenient one-pot wet chemical route. The composition and alloyed structure of the as-prepared nanoparticles were fully characterized. We have evaluated the catalytic activity of these Pd-Au alloy catalysts in Buchwald–Hartwig reactions of aryl chlorides. The excellent catalytic activity of the as-obtained Pd-Au nanoparticles indicates that exploiting the catalytic power of nano-alloy catalysts could enable effective C–Cl bond activation suitable for cross-coupling reactions.

Aromatic amine compounds widely exist in bioactive substances and drugs. They are also widely used in medicines, agricultural pesticides, dyes, pigments, synthetic rubber, etc.^[1-4] Thus, the synthesis of compounds containing a C–N bond has aroused the interest of many researchers. In the past twenty years, palladium-catalyzed coupling reactions of halogenated aromatics and nitrogen-containing compounds in organic synthesis have been widely used. Homogeneous Pd catalysts have been well developed in coupling reactions.^[5-8] The Pd metalligand complex, usually made up of a Pd with N,^[9] O,^[10] and P^[11] donor ligands, could provide high activity and selectivity in the Buchwald–Hartwig reaction of aryl halides due to the geometric and electronic contributions of these ligands to the central Pd active site. The use of homogeneous Pd catalysts

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This manuscript is part of a special issue on catalysis and transformation of complex molecules. Click here to see the Table of Contents of the special issue. limits their applications due to the difficulty to recycle them. Therefore, in recent years, great efforts have been devoted to the development of highly active and selective heterogeneous catalysts.^[12–14] Supported Pd nanoparticles could be easily recycled, but the catalytic efficiency of the catalysts is lower. Accordingly, the heterogeneous Pd catalyst cannot achieve effective results.^[15–19] Furthermore, the activation of an aryl chloride is always difficult to solve. However, compared to bromides and iodides, chlorinated aromatic compounds are easier to obtain and cheaper. Therefore, the use of chlorinated aromatics in the Buchwald–Hartwig coupling is desirable.^[20–22] Hence, it is of great importance and challenging to design and develop new types of heterogeneous catalysts that are able to catalyze the Buchwald–Hartwig reaction of aryl chlorides with high efficiency and durability.

Bimetallic nanocrystals (NCs) are emerging as more important materials than monometallic NCs.^[23–27] They are expected to display not only a combination of the properties associated with the two distinct metals but also new properties and capabilities due to a synergy effect between the two metals.^[28–34] It is essential to prepare bimetallic nanocatalysts with a specific composition, structure, and size for their application in industrial catalysis and to study the mechanism of the catalysis. The focus on PdAu catalysts has been improved in recent years, as they were found to be superior to pure Pd- and Au-supported catalysts in various reactions as hydrogenation,^[25–28] oxidation^[36] and activation of the C–Cl bond.^[12,22]

Herein, we report on the preparation of Pd-Au bimetallic nanoalloys via an easy solution-based method. These bimetallic nanocrystals can be used as an effective and robust catalyst for the Buchwald–Hartwig reaction of aryl chlorides. The catalyst exhibits a high activity and excellent stability with a broad substrate scope and functional group tolerance.

In the synthesis of Pd and Au NPs as well as PdAu BNPs, Pd(acac)₂ (acac=acetylacetonate) and aqueous HAuCl₄ were used as the precursors. Oleylamine (OAm) was used as the solvent and surfactant. Both of the precursors were dissolved in OAm at 60 °C and reduced by borane-*tert*-butylamine at 80 °C. The transmission electron microscopy (TEM) images of the asprepared PdAu BNPs show that all of the BNPs are monodisperse particles with an average size of about 2 nm (Figure 1 b). When Pd(acac)₂ was used as the only precursor, Pd NPs with a particle size of about 3 nm were obtained (Figure 1 a); when aqueous HAuCl₄ aqueous was used as the only precursor, Au



Figure 1. TEM images of Pd NPs (a), PdAu (b), and Au (c); scale bar = 20 nm. (d) XRD patterns of Pd/C, PdAu/C and Au/C.

NPs with a particle size of about 4 nm were produced (Figure 1 c).

The powder X-ray diffraction (XRD) patterns of the as-prepared PdAu BNPs are shown in Figure 1 d. The shift of the (111) diffraction peak corresponding to Pd towards that of Au in the presence of gold demonstrates the formation of the bimetallic structure of the obtained NPs. The high-resolution TEM (HRTEM) image (Figure 2 b) shows the lattice fringes with an interfringe distance of 0.275 nm, which is between the characteristics of Pd and Au crystal phases in the (111) plane, indicating the formation of Pd-Au alloys. The energy-dispersive X-ray



Figure 2. (a) High-angle annular dark-field (HAADF) STEM image of PdAu NCs. (b) HRTEM image of PdAu NCs. (c) EDX elemental maps for Pd (d) and Au (e).

spectroscopy (EDS) mapping profile provides evidence of a homogeneous distribution of palladium (Figure 2d) and gold (Figure 2e) in bimetallic Pd-Au nanoparticles (Figure 2c). The Pd:Au atomic ratio determined by EDX analysis is 34:66 (Figure S1, Supporting Information), which is in good agreement with the result obtained from inductively coupled plasmamass spectrometry (ICP-MS) analysis (Pd:Au = 39:61). The atomic ratio of the products is 1:2 (Pd:Au) which is similar to the proportions of their precursors.

PdAu nanoparticles have been validated to be outstanding catalysts for the activation of C–Cl in the Ullmann coupling reaction; however, other coupling reactions catalyzed by PdAu have not been studied. We therefore explored the catalytic activity of the as-prepared PdAu nanoparticles in Buchwald–Hartwig reactions, especially in the conversion of chlorobenzene.

Using chlorobenzene **1a** and aniline **2a** as the model substrate for Buchwald–Hartwig reactions, we started our initial evaluation of the PdAu NPs (Table 1). The reaction was first

Table 1. Buchwald–Hartwig reaction of chlorobenzene 1 a and aniline over nano PdAu catalyst under various conditions. ^[a]										
$ \bigcirc \overset{CI}{\longrightarrow} \overset{NH_2}{\longrightarrow} \overset{cat.}{\longrightarrow} \overset{N}{\longrightarrow} \overset{N}{\longrightarrow} \overset{V}{\longrightarrow} \overset{V}{\to} \overset{V}{\to}$										
1a	2a	:	3aa	4aa	5	aa				
Entry ^[a]	Solvent	Base	T [°C]	Conv. [%] ^[b]	Sel. [%	6] ^[b]				
					3 aa	4aa	5 aa			
1	toluene	K ₂ CO ₃	80	-	Trace	-	-			
2	toluene	KOH	80	3	Trace	-	-			
3	toluene	Cs ₂ CO ₃	80	-	Trace	-	-			
4	toluene	NaOMe	80	5	80	20	-			
5	toluene	NaOEt	80	2	79	21	-			
6	toluene	KO <i>t</i> Bu	80	10	82	18	-			
7	<i>p</i> -xylene	KO <i>t</i> Bu	80	3	56	44	-			
8	1,4-dioxane	KO <i>t</i> Bu	80	2	43	57	-			
9	DMF	KO <i>t</i> Bu	80	9	52	48	-			
10	DMSO	KO <i>t</i> Bu	80	59	74	16	10			
11	NMP	KO <i>t</i> Bu	80	10	79	21	-			
12	DMA	KO <i>t</i> Bu	80	20	75	25	-			
13	p-xylene/1,4-dioxane	KO <i>t</i> Bu	80	3	76	24	-			
14	DMSO	KO <i>t</i> Bu	90	89	76	13	11			
15	DMSO	KO <i>t</i> Bu	100	>99	89	9	2			
16	DMSO	KO <i>t</i> Bu	110	>99	82	11	7			
17 ^[c]	DMSO	KO <i>t</i> Bu	100	1.2	92	8	-			
18 ^[d]	DMSO	KO <i>t</i> Bu	100	-	-	-	-			
19 ^[e]	DMSO	KO <i>t</i> Bu	100	3.3	90	10				
[a] Table 1 condition: 1 a, 0.5 mmol; 2 a, 1 mmol; 3 mol% catalyst (based										

on metal); KOtBu, 1.5 mmol;solvent, 4 mL; time,12 h. [b] determined by GC with *n*-decane as an internal standard. [c] 3 mol% of Pd was used. [d] 3 mol% of Au was used. [e] 3 mol% of Pd + Au was used.

tested using K_2CO_3 as base in toluene at 80 °C. Only trace amounts of cross-coupling products were formed after 12 h (Table 1, entry 1). Other insoluble bases also did not result in any transformation (Table 1, entries 2–3). Obvious conversion can be observed when alkoxide was used as base (Table 1, entries 4–6) in toluene, and KOtBu gave 10% conversion and 82% selectivity, albeit accompanied by 18% benzene as by-

Chem. Asian J. 2016, 11, 351 – 355

www.chemasianj.org



product for the dehalogenation of chlorobenzene. The good solubility of the alkoxide base may have led to the conversion of the substrate, and a much higher yield was achieved with DMSO as solvent (Table 1, entry10), compared with other solvents (Table 1, entries 7-13). The conversion increased with elevated temperature (Table 1, entry 10 and entries 14-16) and an improved selectivity was obtained at 100°C (89%, Table 1, entry 15). Only little coupling product, diphenylaniline was obtained when monometallic Pd was used as the catalyst (entry 17) and no product was found when monometallic Au was used as the catalyst (entry 18). Furthermore, a slightly increased conversion was obtained when a mixture of monometallic Pd and Au was used. Triphenylamine was obtained because of the further reaction of chlorobenzene with diphenylamine.

As the product of the primary amine can further react with chlorobenzene in a coupling reaction, we assumed that a higher yield could be obtained when a secondary amine and chlorobenzene are used as substrates. Thus, we further investigated the scope of halogenated aromatics that could be tolerated in the Buchwald-Hartwig reaction with a secondary amine (morpholine, Table 2) under the optimized reaction conditions. The coupling of chlorobenzene (1 a) proceeded smoothly to yield N-phenylmorpholine (3 ab) in 97% yield (entry 1). Chloroarenes containing electron-donating groups also reacted under the current reaction conditions. 4-Chloroanisole (1b) and 4-chlorotoluene (1c) were each coupled with morpholine (2b) under the current conditions to give 3bb and 3cb in yields of 96% and 95%, respectively (Table 2, entries 1 and 7). Chloroarenes with an electron-withdrawing group in the para-position (1 d) also underwent coupling well to afford the desired products (Table 2, entry 13). The PdAu nano-alloy catalyst was also tolerant to bromobenzene (1e) and iodobenzene (1 f), and the reaction could proceed smoothly to afford the desired products (Table 2, entries 16

and 17). Next, we checked the catalytic activity of the above chlorobenzenes bearing different substituents with other amines. To our satisfaction, high catalytic activities were observed for both aliphatic amines (Table 2, entries 2, 3, 8 and 14) and aromatic amines (Table 2, entries 4 and 5), affording the corresponding C-N coupling compounds in excellent yields under the optimized reaction conditions. For example, 94% conversion and 94% selectivity towards N,N-dibutylaniline (3 bc) could be obtained when 4-chloroanisole (1 b) was reacted with di-n-butylamine (2c); N-phenylpiperidine (3ad) with 93% selectivity could be obtained when chlorobenzene (1a) was reacted with piperidine (2d). Also N-methylaniline (2e) and N-ethylaniline (2 f) can give 94% and 91% selectivity, respectively, upon coupling with chlorobenzene (1 a). The observed slightly decreased yield of triphenylanilines may be because of sterical hindrance, and a longer reaction time (24 h) is

under optimized conditions. ^[a]								
	$R^{1} \xrightarrow{X} R^{2} NHR^{3} \xrightarrow{PdAu, KOtBu} R^{1} \xrightarrow{R^{2}} R^{2} R^{3}$							
Entry ^[a]	1 R ¹ X	2 R ² R ³ NH	3 Conv. [%] of 1 ^[b]	Sel. [%] of 3 ^[b]				
1		Morpholine (2 b)	> 99	96				
2		N,N-Dibutylaniline (2 c)	> 99	95				
3		Piperidine (2 d)	98	93				
4		N-Methylaniline (2 e)	93	94				
5		N-Ethylaniline (2 f)	91	91				
6 ^[c]		Diphenylaniline (2 g)	83	96				
7	CI	Morpholine (2 b)	96	95				
8	OMe	<i>N</i> , <i>N</i> -Dibutylaniline (2 c)	94	94				
9 ^[c]	1b	Diphenylaniline (2 g)	81	83				
10		Morpholine (2 b)	98	91				
11		<i>N</i> , <i>N</i> -Dibutylaniline (2 c)	99	93				
12 ^[c]		Diphenylaniline (2 g)	80	89				
13	Cl	Morpholine (2 b)	98	94				
14	F	<i>N,N</i> -Dibutylaniline (2 c)	90	92				
15 ^[c]	Id	Diphenylaniline (2 c)	82	82				
16	Bromobenzene	Morpholine (2 b)	>99	92				
17	Iodobenzene	Morpholine (2 b)	>99	94				

Table 2. Scope of the Buchwald-Hartwig reaction catalyzed by nano PdAu catalyst

[a] Table 2 condition: **1a**, 0.5 mmol; **2a**, 1 mmol; 3 mol% catalyst (based on metal); KOtBu, 1.5 mmol; solvent, 4 mL; time, 12 h. [b] determined by GC with n-decane as an internal standard. [c] 24 h is needed.

needed to obtain higher conversion (Table 2, entries 6, 9, 12, and 15).

To understand the chemical state of PdAu in the activation of C–Cl bonds, we referred to X-ray photoelectron spectroscopy (XPS) to inspect the interaction between the two metals. As shown in Figure 3, the XPS spectra show that the binding energies of Pd $3d_{5/2}$ and Pd $3d_{3/2}$ peaks are located at 336 eV and 341.2 eV, respectively, which are slightly shifted to the higher side in binding energy. By comparison, the Au $4f_{7/2}$ and Au $4f_{5/2}$ peaks of PdAu are shifted obviously to the lower side in binding energy. This tendency indicates that the Au atoms gained electrons from Pd atoms by alloying interaction. Based on the charge compensation concept, Pd atoms in PdAu may have electronic poor states which may play a crucial role in the activation of C–Cl bonds or the enhancement of reaction pathway of cross-coupling, leading to the high activity.

Chem. Asian J. 2016, 11, 351 – 355

www.chemasianj.org



Figure 3. XPS spectra of Pd 3d and Au 4f peaks of (a) Pd, (b) PdAu₂ 4f XPS and (c) Au.

 $80 \degree C$ for a further 1 h. After cooling to room temperature, the solution was washed with ethanol (40 mL×3) and then dispersed in cyclohexane for future use.

For the preparation of Pd/C, PdAu/ C, and Au/C catalysts, activated carbon was added into the dispersions of Pd, PdAu, and Au at a loading of 3 wt.% (based on Pd and Au), and the mixtures were stirred overnight. The catalysts were obtained through centrifugation and drying under vacuum.

The PdAu bimetallic catalyst can be easily recovered and reused in the Buchwald–Hartwig reaction of 4-chloroanisol for three times without any obvious loss of efficiency (see the Supporting Information). The liquid phase of the reaction mixture was collected by hot filtration after the reaction and analyzed by ICP-MS. A very low amount of dissolved palladium (less than 0.2% of the total palladium) was detected in the solution at the end of the reaction. Moreover, the catalyst was removed from the solution after approximately 50% conversion at the reaction temperature. The isolated solution did not exhibit any further reactivity under similar reaction conditions. These studies indicate that the reaction was intrinsically catalyzed by a heterogeneous catalyst.

In conclusion, we have developed a highly efficient heterogeneous catalyst system for the Buchwald–Hartwig reactions of aryl chlorides using PdAu bimetallic NPs as the catalyst. Furthermore, the catalyst is stable, shows negligible metal leaching, and maintains high catalytic activities over a number of cycles. The use of PdAu as catalyst further verifies the excellent opportunities in the development of highly active heterogeneous catalysts for C–N coupling or other palladium-catalyzed coupling reactions, especially with regard to the activation of C–Cl bonds. Studies aimed at extending the scope of PdAu NPs to other organic transformations are currently underway in our laboratories.

Experimental Section

Chemicals

 $Pd(acac)_2$ and $HAuCl_4$ were obtained from Alfa Aesar, oleylamine (OAm) was purchased from J&K Chemical, and activated carbon was obtained from TCI. Other analytical-grade solvents were purchased from Beijing Chemical Reagents. All of the chemicals were used without further purification.

Synthesis

In a typical preparation of PdAu nanocrystals, 0.1 g L⁻¹ aqueous HAuCl₄ (270 μ l) and Pd(acac)₂ (10 mg) were dissolved in OAm (10 mL) at 60 °C under vigorous stirring for 10 min. Then, a solution of borane-*tert*-butylamine (100 mg, 1.15 mmol) in OAm (1 mL) was added quickly into the previous solution, and the reaction mixture immediately turned black. After 1 min, the flask was heated to

Characterization

Powder XRD patterns were recorded with a Bruker D8 ADVANCE Xray powder diffractometer with Cu_{Ka} radiation ($\lambda = 1.5406$ Å). The sample compositions were determined by EDX, and the particle size and dispersion were investigated with a Hitachi H-800 transmission electron microscope (TEM). X-ray photoelectron spectroscopy (XPS) was conducted with a Thermo Fisher ESCALAB 250Xi spectrometer equipped with a monochromatic AI X-ray source.

Catalytic Properties

For a typical run, chlorobenzene (0.5 mmol), aniline (1 mmol), KOtBu (1.5 mmol) and PdAu catalyst (3 mol% of chlorobenzene based on Pd and Ag) were placed in a 10 mL flask with DMSO (4 mL) as the solvent. The reaction was performed in an oil bath at the specified temperature. Liquid samples were analyzed by gas chromatography using a Thermo Finnigan chromatograph equipped with a flame ionization detector and a DB-WAX capillary column (J&W, 30 m, 0.25 mm i.d.) with nitrogen as the carrier gas.

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Chem. Asian J. 2016, 11, 351 – 355

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354

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