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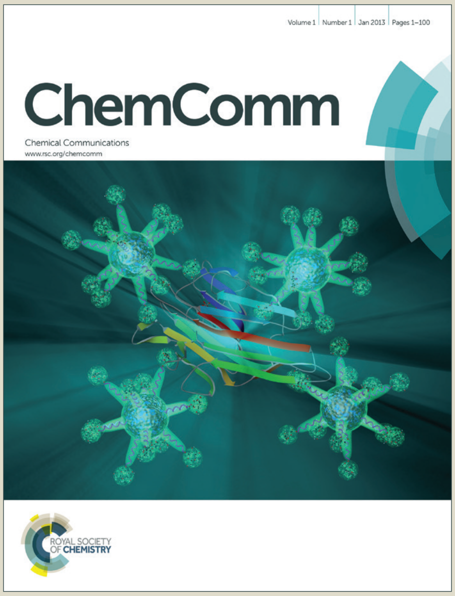

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Significant Stabilization of Palladium by Gold in the Bimetallic Nanocatalyst Leading to an Enhanced Activity in the Hydrodechlorination of Aryl Chlorides

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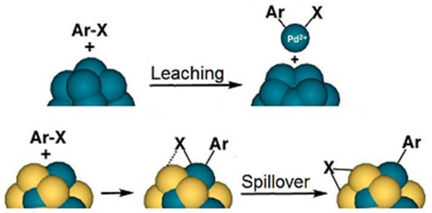
The stabilization effect of Au towards Pd changed the reactivity of Pd in Au/Pd bimetallic nanoclusters, altering the reaction mechanism from homogeneous to heterogeneous in dechlorination reaction of aryl chlorides. This phenomenon was illustrated by observed enhancement of rate of reaction by *in-situ* generated Au-rich bimetallic Au/Pd nanoclusters.

Catalysis by palladium nanoparticles (NPs) has aroused great interest because of its widespread applications in organic synthesis, including C–C bond-forming reactions. The nature of the active catalytic species in such reactions as the Mizoroki–Heck[1] and Suzuki–Miyaura[2] coupling reactions has been a mostly focused issue since the past several decades. Most of the C-C coupling reactions are found to be catalyzed by soluble palladium complexes following usual homogenous mechanism.[3,4d,5a,9] Leaching of Pd in the coupling reactions has already been well-established as demonstrated by various experimental approaches.[9a] It has been reported that leaching of Pd species from the surface of a catalyst through oxidative addition of aryl halides gives ArPdX species that react homogenously, forming the desired product and Pd^0 species (scheme 1). The resulting Pd^0 species can react further or they can redeposit on the cluster surface.[4-6] Alternatively, in the absence of a strong ligand or stabilizer, they can be deactivated through the formation of Pd black.[4] It is a major limitation of Pd NPs chemistry in coupling reactions because once oxidative addition happens, Pd^{2+} will form and it will no longer stay on the surface. Stabilization of such active palladium species either in solution or on heterogeneous surface is a quite difficult task. From the last few decades, researchers have been paying much effort on developing new strategies for designing high performance heterogeneous catalysts to prevent the usual homogenous coupling mechanism by developing immobilizing protocols.[7] Recent publications on coupling reactions utilizing catalysts such as Pd grafted on mesoporous material[7a,b,f] or zeolites[7c] and Pd on HAP macroligand[7d,e] assure to compete the usual homogenous mechanism. However, such strategies are limited and a new and simple strategy to develop the efficient heterogeneous catalytic system that can promise to prevent leaching, agglomeration and deactivation of catalyst is essential.

Bimetallic nanoparticles have attracted attention because of their enhanced catalytic activities, selectivities, and stabilities in comparison to their single-metal counterparts.[10] Especially, Au/Pd bimetallic alloy has superior catalytic activities in various types of reaction under mild conditions.[11–17] The activity and selectivity of Pd catalyst can be enhanced by alloying with Au due to the synergistic effects of bimetallic surfaces,[16d–e] such as ensemble and the ligand effect.[10b] Furthermore, bimetallization can result in stabilization of nanoparticles in cases where one metal acts as stabilizer for the other, preventing aggregation.[10b,16e,16f]

In our previous report, we observed unique catalytic activity of *poly*(N-vinylpyrrolidone) (PVP)-stabilized Au/Pd bimetallic nanoparticles[17] for C–Cl bonds activation in Ullmann coupling reactions of chloroarenes[17a] and the unusual Suzuki-Miyaura-type coupling reaction.[17b] Through DFT calculation of the reaction mechanism, we realized that spillover of Cl over gold is a crucial step in the reaction, that drives the reaction through



Scheme 1. Proposed oxidative addition mechanism on Pd

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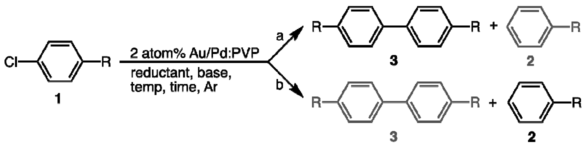
heterogeneous path preventing the homogeneous path (scheme 1).[17a,18] The best conditions for activation of C–Cl bonds for C–C bond-formation reactions involved the use of N,N-dimethylformamide (DMF) as solvent and hydrogen donor (Scheme 2, Conditions a; Table 1, entry 1). So, we expected that the use of other reducing solvents, such as alcohols (Scheme 2; Conditions b), would result in selective activation of the C–Cl bond towards hydrodechlorination. Similar alteration of product selectivity of the two competing process based on concentration of reductant has been well discussed by Sasson and coworkers.[8]

In the course of our study to elucidate the stabilizing effect of gold toward palladium, we chose the hydrodechlorination reaction as our model reaction because, for Pd, it is difficult to activate C-Cl bond and once, it is activated, Pd may be released as Pd (II) ion in solution due to oxidative addition process (scheme 2). To this species, the second oxidative addition process is very difficult and it is quite impossible to get the Ullmann coupling product due to low nucleophilicity on Pd and strong electrophilicity of C-Cl bond.[17a] Instead, if we use the hydride source, it will possibly undergo reduction, giving arene as the product even through usual homogenous mechanism and release the Pd^0 which can be captured by Au as a stabilizing ligand. Au is the best choice among other metals to capture Pd because of the similar lattice constant and low energy demand for bimetallization.[16e-h] Besides, the nucleation process of Pd is relatively slow.[16i] In this work, we attempt to release Pd and trap it by Au during hydrodechlorination reaction and tune the reaction mechanism from homogenous to heterogeneous.

First, to identify optimal conditions for the dechlorination dechlorination, the reaction of 1-chloro-4-methoxybenzene (**1**) was carried out in the presence of Au/Pd:PVP as a catalyst and potassium hydroxide as the base in dimethyl sulfoxide (DMSO), no reaction occurred because of the nonreducing nature of the solvent (entry 2). However, the yield of dechlorination product methoxybenzene (**2**) increased in alcohol solvents. Reactions in 1:1 mixtures of methanol, ethanol, or propan-2-ol with water gave 2 in yields of 22%, 63%, and 70%, respectively (entries 3–5) and without water in ethanol (78%) and propanol (>95%) (entries 6–7). The best conditions involved the use of anhydrous propan-2-ol as the sole solvent; under these conditions, the reaction was completed within one hour at 45 °C and five hours at 25 °C giving >95% yield of **2** (entry 7-8). The optimized or slightly modified reaction conditions were applied to the dechlorination of various substrates including polychlorinated compounds and the results are summarized in Table S1 (ESI).

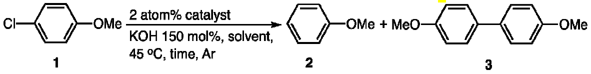
The efficiency of various Au and Pd catalysts for the dechlorination reaction was compared by performing the reaction of 1-chloro-4-methoxybenzene (**1**) for 1 h (Table 1). The highest catalytic activity was shown by Au/Pd bimetallic alloy nanoparticles, which gave **2** quantitatively (Table 1, entry 7). The dechlorination reaction of **1** did not proceed when Au:PVP was used as a catalyst (entry 9), whereas Pd:PVP did give **2**. When Pd:PVP was used as a catalyst under the same conditions, the yield of **2** was only 24% (entry 10), while the physical mixture of the two monometallic catalysts Au:PVP and Pd:PVP (Au + Pd) gave 51% yield, which was higher than that obtained with Pd:PVP alone (entry 11). To test the effect of Au on the catalytic activity of Pd, we performed the reaction under identical conditions using physical mixtures of the two monometallic catalysts in varying Au and Pd ratios (Figure S1, ESI). Even a small amount of Pd in Au, or vice versa, enhanced the catalytic activity to a value higher than that displayed by Au or Pd alone.



Scheme 2. C-Cl bond activation by Au/Pd:PVP catalyst

Measurements of the kinetics of consumption of **1** (Figure 1) showed differences in the catalytic activities of Au/Pd alloy, Pd, and (Au + Pd) nanoparticles. The reaction with bimetallic Au/Pd:PVP was a very fast second-order reaction with a rate constant for consumption of **1** of k = 5.6 × 10–1 $Lmol^{-1}h^{-1}$ (Figure S2, ESI). The reaction with monometallic Pd:PVP, on the other hand, was very slow and showed first-order kinetics. The 1:1 physical mixture of Au:PVP and Pd:PVP show a reactivity that was intermediate between those of the two monometallic catalysts. At the beginning of the reaction, the catalytic activity of Pd:PVP (2 atom%) was higher, and the reaction rate was almost double than that observed with Au:PVP (1 atom%) + Pd:PVP (1 atom%) mixture. However, after two hours, the activity of the Au + Pd mixture gradually increased in comparison to that of Pd alone. The kinetic of consumption of 1 in the presence of the Au + Pd mixture at 25 °C showed a linear fit to the first-order plot of –ln[A] versus time, with an observed rate of consumption of **1** (k_{1a}) = 3.7 × 10^{-2} h^{-1} for the initial 2 hours of reaction. However, the slope then increased significantly, corresponding to an increase in the rate to 4.6 × 10^{-2} h^{-1} and a

Table 1. Optimization of reaction conditions[a]



entry	solvent	t (h)	catalyst	yield (%)[b]	
				2	3
1	DMF-H_2O (1:2)	24	Au/Pd:PVP	6	92
2	DMSO-H_2O (1:1)	24	Au/Pd:PVP	0	0
3	MeOH-H_2O (1:1)	24	Au/Pd:PVP	22	20
4	EtOH-H_2O (1:1)	24	Au/Pd:PVP	63	14
5	*i*PrOH-H_2O (1:1)	24	Au/Pd:PVP	70	17
6	EtOH	24	Au/Pd:PVP	78	11
7	*i*PrOH	1	Au/Pd:PVP	>95	trace
8[c]	*i*PrOH	1	Au/Pd:PVP	>95	trace
9	*i*PrOH	1	Au:PVP	0	0
10	*i*PrOH	1	Pd:PVP	24	0
11	*i*PrOH	1	Au:PVP[d] + Pd:PVP[d]	51	trace

[a] Reaction conditions: 1 (0.1 mmol), catalyst (2 atom%), KOH (150 mol%), solvent (3 mL), 45 °C, under argon. [b] Yield by GC analysis. [c] At 25 °C. [d] 1 atom %.

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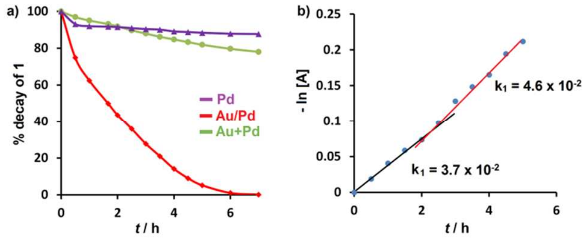


Figure 1. (a) Time-dependent consumption of **1** at 25 °C; Reaction conditions: **1** (0.3 mmol), NaOH (150 mol%), catalyst (2 atom%), *i*PrOH; (b) plot of –ln[A] vs time for Au + Pd

change in the order of the reaction (Figure 1c).

On the basis of the above results, we hypothesized that leaching might occur from the surface during catalysis by monometallic Pd due to oxidative addition of the C–Cl bond. This species must be exclusively responsible for the initial catalytic activity through a homogeneous mechanism because Au:PVP on its own shows no activity in the reaction. In the presence of gold, in situ reduction of Pd(II) under the reaction condition might lead to the Au/Pd bimetallic catalyst with high dispersion of Pd on Au (Table 1, entry 11). We therefore propose the existence of two catalytic cycles for the observed reactivities of monometallic and bimetallic nanoparticles, respectively, (Scheme 3). The catalytic reaction involving the bimetallic nanoparticles follows a heterogeneous mechanism and occurs on the surface of the catalyst (cycle A) because of the spillover of Cl over gold. The process is very fast, with no aggregation or deactivation of the catalyst at any stage of the reaction. In the case of monometallic Pd:PVP in the absence of Au, the catalyst shows a homogeneous reaction mechanism (cycle B) through leached Pd. This is a slow process and, as the reaction proceeds, the Pd^0 species becomes gradually deactivated through aggregation, with the formation of Pd black. In the presence of Au, however, the leached palladium species that are present in solution are captured by Au to form bimetallic Au/Pd:PVP And both catalytic cycles operating simultaneously in the case of physical mixtures of Au:PVP and Pd:PVP.

To verify our hypothesis, we used transmission electron microscopy (TEM) to examine structural and morphological changes in the metal nanoparticle as a result of the reaction. The two monometallic nanoparticles Au:PVP and Pd:PVP were mixed in a 1:1 ratio, and TEM images were recorded before and after the reaction (Figure S3 and S4, ESI). The images taken before reaction showed the Au:PVP and Pd:PVP nanoparticles separately, with average sizes of 1.6 ± 0.4 nm and 3.9 ± 0.6 nm, respectively. However, images

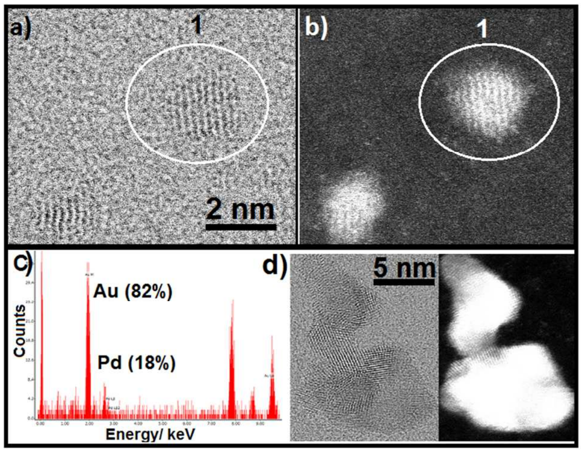
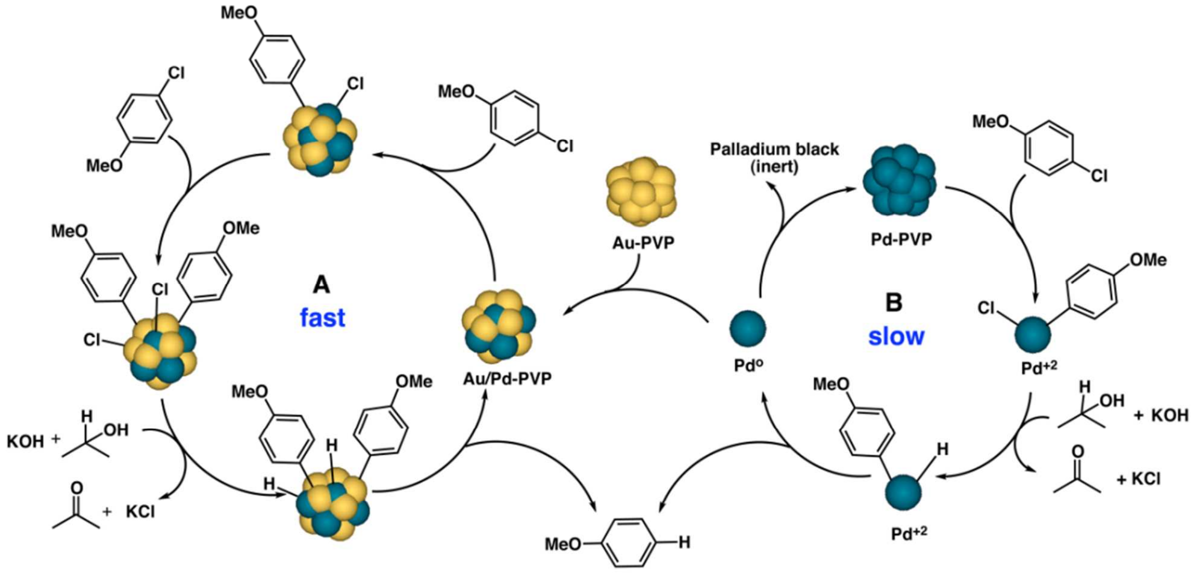


Figure 2. a) Bright-field and b) high-angle annular dark-field (HAADF) STEM images of particle 1 after reaction. c) STEM-EDX spectrum of particle 1. d) Bright-field (left) and HAADF STEM images of a polymorphic particle formed after reaction**.**



Scheme 3. Proposed catalytic cycles A (Heterogeneous) and B (Homogeneous) for the dechlorination reaction

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recorded after the reaction showed morphological changes, with a growth in the size of the nanoparticles. Detailed scanning transmission electron microscopy (STEM) energy dispersive X-ray spectroscopy (EDX) measurements showed that most of the particles are polymorphological with non-uniform lattice pattern. However, it revealed the existence of some of bimetallic nanoparticles containing various amounts of Au and Pd (Table S2, Figure S5, ESI). These particles show uniform lattice pattern and single crystallinity but possessing two metals (Figure 2). This supports our belief that the enhanced catalytic activity of Pd is due to the dilution of surface Pd atoms by gold in forming these very few numbers of Au rich Au/Pd bimetallic nanoparticles *in situ*.

In summary, through the result of hydrodechlorination reaction reaction we could clearly conclude the leaching of Pd species; these enhance the catalytic activity by interacting with the Au nanoparticles in Au/Pd bimetallic nanoparticles generated *in situ* and the heteroatomic gold drives the reaction mechanism from homogeneous to heterogeneous. This phenomenon provides a good illustration of a bimetallic effect in which one metal dopes another metal. We also found that Au plays two important roles. The first is to capture and stabilize Pd, and the second is to produce a bimetallic system that catalyzes the reaction by a different mechanism.

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Table of contents

The stabilization of Au by Pd in Au/Pd bimetallic nanoclusters enhanced the reactivity of Pd and changed the reaction mechanism.