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$PdCu/Al_2O_3$ catalyst for Sonogashira cross-coupling: effect of a Pd/Cu ratio on the catalytic performance

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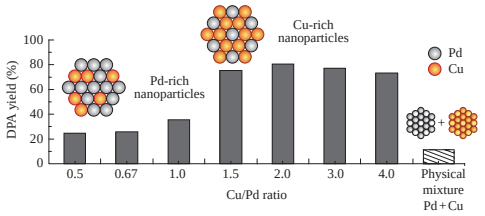
The catalytic performance of 3 wt% Pd–Cu/Al_2O_3 containing bimetallic alloy Pd–Cu nanoparticles strongly depends on the Pd/Cu ratio in the cross-coupling of phenylacetylene with phenyl iodide, and a maximum activity is attained at Pd/Cu = 1:2.



The Sonogashira reaction, which is based on the cross-coupling of an aryl or vinyl halide with a terminal alkyne, is a powerful tool for the synthesis of precursors for agrochemicals and pharmaceuticals, natural products and materials with valuable optical or electronic properties.[1,2] Aryl-substituted alkynes can be easily synthesized *via* the Sonogashira coupling reactions in the presence of a palladium catalyst and a copper co-catalyst to achieve a good yield.[3,4] The presence of copper is essential since copper plays an important role in transferring the alkynyl group to palladium, thus significantly facilitating the overall process.[5] On the other hand, the use of copper as a co-catalyst can result in the formation of homocoupling products of the terminal alkyne along with the desired coupling product, and it requires the utilization of an environmentally unfriendly CuX.[6]

These serious drawbacks can be avoided or minimized by applying supported Pd–Cu bimetallic nanoparticles. Recently, it was found that the modification of Pd nanoparticles with Cu significantly enhances the catalytic performance of Pd catalysts in Suzuki–Miyaura, Heck and Sonogashira carbon–carbon coupling reactions.[7–11] Heterogeneous catalysts containing Pd–Cu nanoparticles offer significant advantages over Pd–Cu homogeneous catalytic systems. The former are environmentally friendly and demonstrate high activity allowing one to enhance the target product yield and to reduce palladium loading, and make possible easy separation of the catalyst from reaction products. All of these characteristics are of importance for modern chemistry.[12]

An important factor affecting the performance of Pd–Cu bimetallic catalysts is the Pd/Cu ratio. The nanocatalyst with Pd/Cu = 4:1 showed the highest activity in the C–C Heck coupling reaction of iodobenzene with styrene.[13] Catalytic performance of Pd–Cu nanoparticle was also studied in the Suzuki–Miyaura reaction between phenylboronic acid and halobenzenes (iodo-, bromo- or chlorobenzene) and the Cu-rich Pd–Cu_3 nanocatalyst demonstrated the best efficiency.[7] However, the effect of this parameter on the performance of the Pd–Cu catalyst in the Sonogashira cross-coupling remains unclear. A series of supported Pd–Cu/MgO catalysts and mixed Mg–Al hydrotalcite with different Pd/Cu ratios has been examined;[14] however, in these experiments, both Pd and Cu contents were varied within a broad range (from 0.2 to 5 wt% for Pd and from 1.6 to 3.6 wt% for Cu), which makes it difficult to evaluate the effects of Pd/Cu ratio and Pd loading.

This study was focused on the revealing the effect of the Pd/Cu ratio on the performance of Pd-Cu/Al_2O_3 in the Sonogashira cross-coupling of phenylacetylene with phenyl iodide as a model reaction. To achieve this goal, a representative series of Pd–Cu catalysts with a constant palladium loading (3 wt%) was prepared by varying the Pd/Cu molar ratio from 1:0.5 (Pd-rich catalyst, designated as Pd_1–$Cu_{0.5}$) to 1:4 (Cu-rich catalyst designated as Pd_1–Cu_4). The catalysts were prepared by the incipient-wetness impregnation of α-Al_2O_3 with the solutions of corresponding Pd and Cu salts. The choice of α-Al_2O_3 as a carrier was dictated by its low specific surface area and a wide-porous structure, which makes α-Al_2O_3 ideal for liquid-phase reactions since its porous structure minimizes diffusion effects on the reaction kinetics. The formation of Pd–Cu bimetallic alloy nanoparticles was confirmed by X-ray diffraction (XRD) and transmission electron microscopy (TEM) which are usually successfully used for evaluating the morphology and structure of intermetallic compounds.[15,16] The performance of a catalyst containing Pd–Cu nanoparticles with an optimal Pd/Cu ratio was compared with that of the catalyst prepared by the mechanical mixing of individual Pd/Al_2O_3 and Cu/Al_2O_3 in order to estimate the importance of proximity between palladium and copper components for the catalytic characteristics.†

Figure 1 shows the XRD patterns of Pd-Cu/Al_2O_3 and monometallic Pd/Al_2O_3 and Cu/Al_2O_3 samples. The diffraction peaks at 40.5, 47.0 and 67.8° (not shown) were detected in the monometallic palladium sample ascribing (111), (200) and (220) lattice planes of face-centered cubic palladium lattice structures.[17] Similarly, the Cu/Al_2O_3 catalyst showed low-intense reflexes at 51 and 74° (not shown) attributable to the crystal planes of Cu (200) and (220), respectively.[18,19] Note that no distinct signal was observed for Cu/Al_2O_3 catalyst at ~43.3°, which is characteristic of Cu (111) crystal planes. Presumably, this peak is overlapped with the intense reflex of α-Al_2O_3 at 43.7°. For

† Experimental details of catalyst preparation, catalytic tests and characterization by XRD and TEM can be found in Online Supplementary Materials.

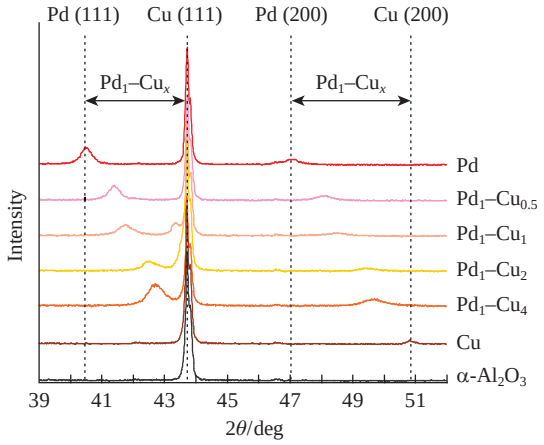


Figure 1 XRD patterns of Pd–Cu/α-Al_2O_3 with different Pd/Cu ratios.

Pd–Cu catalysts, XRD reflexes are located between those of monometallic fcc Pd and Cu. In comparison with palladium pattern, the diffraction signals of Pd–Cu samples upshifted toward higher angles with increasing the Cu content from ~41 to ~43 and from ~48 to 50% for Pd_1–$Cu_{0.5}$ and Pd_1–Cu_4, respectively. Thus, the modification of a Pd catalyst with copper leads to the contraction of the crystal lattice and clearly indicates the formation of Pd–Cu alloy with fcc structure.[20,21] Neither Pd nor Cu diffraction peaks were detected in the Pd–Cu samples confirming that Pd and Cu atoms were completely incorporated into the alloy structure of Pd–Cu nanoparticles. Additionally, the Pd/Cu ratios evaluated in accordance with Vegard's law are consistent with those in the initial precursors. The Pd–Cu reflexes are somewhat asymmetric for the samples with high copper loading indicating the presence of two types of fcc structures in the catalysts.[22]

The morphology of bimetallic Pd–Cu catalysts was characterized by TEM (Figures 2 and S1, see Online Supplementary Materials). Large nearly spherical particles of ~60 nm can be clearly seen in the micrograph of the Pd_1–$Cu_{0.5}$ bimetallic catalyst. As the Pd/Cu ratio was increased from 1:0.5 to 1:2, the size of metal particles remains almost constant (see Figure 2). A further increase in Pd/Cu to 1:3 and 1:4 results in somewhat smaller particle sizes of ~20–25 nm for Pd_1–Cu_3 and Pd_1–Cu_4 (Figures 2 and S1). A similar tendency was observed previously.[17] In accordance with TEM data, we can conclude that the size of Pd–Cu bimetallic clusters can be modified by adjusting the second metal content.

The catalytic performance of the Pd–Cu/Al_2O_3 bimetallic catalysts was evaluated in the model Sonogashira reaction of iodobenzene and phenylacetylene in the presence of pyrrolidine as a base and DMF as a solvent at 80 °C affording diphenylacetylene (DPA) (Table 1, Figures S2 and 3). The reference Pd/α-Al_2O_3 catalyst demonstrates low activity, and the yield of DPA did not exceed 2–3% after 6 h of reaction. The modification of palladium nanoparticles even with a minor amount of copper (Pd_1–$Cu_{0.5}$) significantly improves the catalytic performance, and the DPA yield increased to 24.7% (TOF = 5.3 h^{-1}). A further increase in the Pd/Cu ratio results in a gradual growth of the reaction rate, and

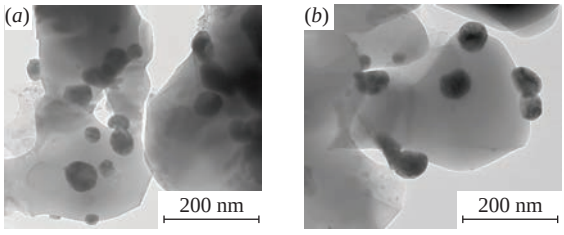


Figure 2 TEM micrographs of the bimetallic Pd–Cu/α-Al_2O_3 catalyst with (*a*) Pd_1–$Cu_{0.5}$ and (*b*) Pd_1–Cu_2 ratios.

Table 1 Catalytic performance of bimetallic Pd–Cu/α-Al_2O_3 catalysts in the Sonogashira coupling of phenylacetylene and iodobenzene.

Catalyst	$D_{Pd–Cu}$[a]/ nm	Cu (wt%)	Reaction time, 2 h		Reaction time, 6 h	
			PhI conversion (%)	DPA yield (%)[b]	PhI conversion (%)	DPA yield (%)[c]
Pd_1–$Cu_{0.5}$	61	0.9	11.9	10.3	28.5	24.7
Pd_1–$Cu_{0.67}$	43	1.2	16.9	14.6	29.1	25.9
Pd_1–Cu_1	46	1.8	19.6	16.0	43.4	35.5
Pd_1–$Cu_{1.5}$	54	2.7	55.8	49.5	84.4	75.3
Pd_1–Cu_2	47	3.6	71.0	63.9	90.0	80.5
Pd_1–Cu_3	21	5.4	66.1	58.4	85.1	77.2
Pd_1–Cu_4	24	7.2	53.7	45.8	82.9	73.3
Physical mixture Pd_1–Cu_1	–	1.8	10.0	5.8	25.2	14.5
Physical mixture Pd_1–Cu_2	–	3.6	5.8	3.0	21.5	11.2
Pd	–	–	1.0	1.1	2.9	2.7
Cu	–	1.8	1.2	0.1	6.4	0.6

[a] Calculated based on the TEM data. [b] Determined by GC. [c] Isolated yield after column chromatography.

TOF steadily increases from 5.3 to 46.8 h^{-1} for Pd_1–Cu_2. Note that the enhancement of the catalytic activity of Pd–Cu/Al_2O_3 is not related to a change in metal dispersion, since the size of Pd–Cu particles is almost identical for Pd_1–$Cu_{0.5}$ and Pd_1–Cu_2 (see Figure 2). This observation suggests that the improved performance stems from the reactivity enhancement of Pd–Cu surface as the Pd/Cu ratio is raised. Pd_1–Cu_2 demonstrates optimal catalytic performance in terms of reaction rate (TOF = = 46.8 h^{-1}) and DPA yield (~81%). This result is consistent with the reported data indicating that Cu-enriched Pd–Cu nanoparticles (Pd/Cu = 1:3) demonstrate the most favorable activity in the Suzuki–Miyaura cross-coupling.[7]

A further increase in the Pd/Cu ratio results in the gradual degradation of the catalytic performance, and the DPA yield for Pd_1–Cu_3 and Pd_1–Cu_4 decreases to 77.2 and 73.3%, respectively, despite a smaller size of metal nanoparticles in these catalysts. The decrease in the DPA yield is accompanied by the increased formation of diphenylbutadiyne, which is the homocoupling product typical of Cu-catalyzed reactions.[23] The degradation of the performance can be explained by the thermodynamically favorable surface segregation of copper atoms,[24] which lowers the availability of palladium active centers and, consequently, decreases cross-coupling reaction rate, and increases the contribution of homocoupling reaction.

It is important that, under identical reaction conditions, the physical mixtures of the monometallic systems (Pd/α-Al_2O_3 and Cu/α-Al_2O_3) are significantly less active (TOF = 17.2 h^{-1}, DPA yield ~11.2%) compared to the most active Pd_1–Cu_2 despite

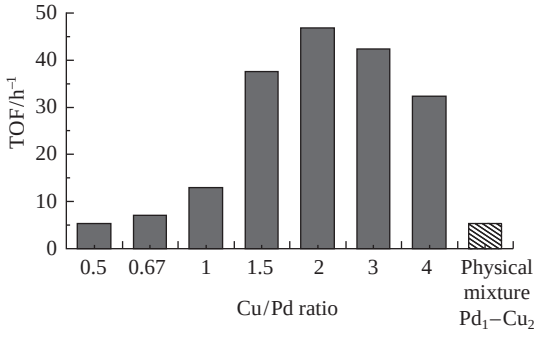


Figure 3 Catalytic activities of Pd–Cu/α-Al_2O_3 bimetallic catalysts with different Pd/Cu ratios in the Sonogashira reaction between phenylacetylene and iodobenzene.

the fact that identical amounts of Pd and Cu were loaded into a reactor in both of the experiments. Moreover, in the case of physical mixtures, significant formation of diphenylbutadiyne as a homocoupling product was observed. Evidently, a higher catalytic efficiency of the bimetallic system as compared to that of the corresponding monometallic Pd and Cu systems and their equivalent physical mixture suggests that the close proximity of Pd and Cu components and their interaction due to Pd–Cu alloy formation is essential for a synergic effect between the two metals, which significantly improves the catalytic performance of Pd–Cu/Al_2O_3 bimetallic catalysts in the Sonogashira reaction.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2018.09.030.

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