

Silica-supported Poly- γ -aminopropylsilane Cu^{2+} - Pd^{2+} Complex: A New Catalyst System for Heck Vinylation Reaction

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Abstract: In this paper, a new silica-supported poly- γ -aminopropylsilane Cu^{2+} - Pd^{2+} complex was studied in Heck vinylation reaction of aryl iodide with olefins. The catalyst is highly active and stereoselective at 70-100 °C, and can be reused after washing without loss in activity.

Keywords: Catalyst, Heck reaction, poly- γ -aminopropylsilane.

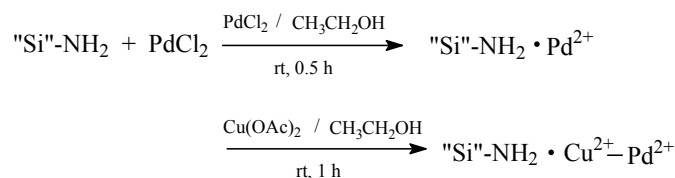
The Heck vinylation of aryl halides, one of the most important C-C bond formation reactions in organic synthesis is mostly catalyzed by homogenous or heterogeneous palladium complexes¹⁻⁴. Comparison with palladium catalysts, transition metal catalysts are much less expensive, but catalytic activity was low and decreased rapidly when it was reused⁵. In this paper, we report the preparation of silica-supported poly- γ -aminopropylsilane Cu^{2+} - Pd^{2+} complex (“Si”- NH_2 - Cu^{2+} - Pd^{2+}). It possesses excellent catalytic activity and stereoselectivity in Heck reactions.

In our study, fumed silica was used as the support. The supported Cu^{2+} - Pd^{2+} complex catalyst could be easily prepared by the reaction of poly- γ -aminopropylsilane with the fumed silica, followed by treatment with $\text{Cu}(\text{OAc})_2$ and PdCl_2 in ethanol (**Scheme 1**). In the complexes, the Cu and Pd contents were 2.48 wt% and 0.25 wt% in “Si”- NH_2 - Cu^{2+} - Pd^{2+} , respectively. Nitrogen content was 3.2 wt%. The Cu content was 2.62 wt% in “Si”- NH_2 - Cu^{2+} , and the Pd content was 2.54 wt% in “Si”- NH_2 - Pd^{2+} .

In the presence of these catalysts, the vinylation reaction of iodobenzene with acid was carried out at 70-140 °C. The reaction progress was monitored by TCL. The results were listed in **Table 1**. From **Table 1**, it was found that these catalysts gave the corresponding *trans*-product in high yields (86-99 %) and the addition of trace palladium in supported copper complex would obviously improved its catalytic activity. Catalytic activity of the supported copper-palladium complex was much higher than that of supported palladium or copper complex, and the sequence of catalytic activity was “Si”- NH_2 - Cu^{2+} - Pd^{2+} > “Si”- NH_2 - Pd^{2+} > “Si”- NH_2 - Cu^{2+} . The result shows that there is a synergetic action between copper and palladium in “Si”- NH_2 - Cu^{2+} - Pd^{2+} catalyst.

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Scheme 1

**Table 1** Effect of temperature on catalytic performance of "Si"-NH₂·Cu²⁺-Pd²⁺*

Catalyst	Aryl iodide	Alkene	Temp.	Yield**(Time, h)
			()	(%)
"Si"-NH ₂ ·Cu ²⁺ -Pd ²⁺	C ₆ H ₅ I	CH ₂ =CHCO ₂ H	70	86(8)
			90	89(1)
			110	96(0.5)
"Si"-NH ₂ -Cu ²⁺	C ₆ H ₅ I	CH ₂ =CHCO ₂ H	120	92(8)
			130	95(3)
			140	88(2)
"Si"-NH ₂ -Pd ²⁺	C ₆ H ₅ I	CH ₂ =CHCO ₂ H	70	90(15)
			90	99(3)
			110	95(1)

*0.05 g catalyst 5 mmol iodobenzene, 5.5 mmol acrylic acid, 3 mL DMF and 2.03 g Bu₃N were used. Product was identified by IR and H NMR. **Isolated yield based on iodobenzene.

The activities of the "Si"-NH₂·Cu²⁺-Pd²⁺ complex were also tested for the vinylation reactions of substituted aryl iodides with a varieties of olefins. All reactions were complete in 1-12 h at 90-100 °C to give the corresponding *trans*-products in high yields (87-95 %) and no *cis*-product was observed. The results were listed in **Table 2**. The catalyst can be easily recovered by simple filtration. Two recycles were carried out for the arylation of acrylic acid with iodobenzene, the yield of *trans*-cinnamic acid did not decrease. The supported copper-palladium complex shows the potential application in Heck reaction in industry.

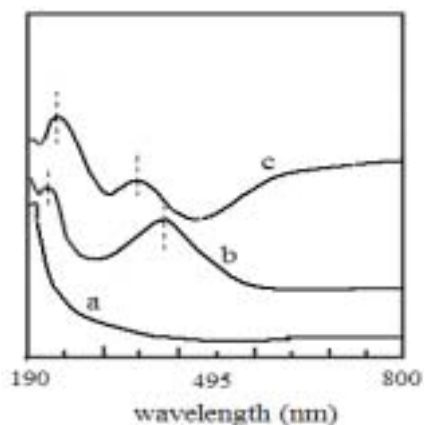
Table 2 Vinylation reactions of substituted aryl iodides with alkenes catalyzed by "Si"-NH₂·Cu²⁺-Pd²⁺*

Aryl iodide	Alkene	Product	Temp.	Time	Yield
			()	(h)	(%)**
C ₆ H ₅ I	CH ₂ =CHCO ₂ H	(E)-C ₆ H ₅ CH=CHCO ₂ H	90	1	89
C ₆ H ₅ I	C ₆ H ₅ CH=CH ₂	(E)-C ₆ H ₅ CH=CHC ₆ H ₅	100	12	87
4-CH ₃ OC ₆ H ₄ I	CH ₂ =CHCO ₂ H	(E)-4-CH ₃ OC ₆ H ₄ CH=CHCO ₂ H	100	10	95
4-CH ₃ OC ₆ H ₄ I	C ₆ H ₅ CH=CH ₂	(E)-4-CH ₃ OC ₆ H ₄ CH=CHC ₆ H ₅	100	12	91
4-COOHC ₆ H ₄ I	CH ₂ =CHCOOH	(E)-4-COOHC ₆ H ₄ CH=CHCO ₂ H	100	12	89
4-COOHC ₆ H ₄ I	C ₆ H ₅ CH=CH ₂	(E)-4-COOHC ₆ H ₄ CH=CHC ₆ H ₅	100	12	87

*0.05 g catalyst 5 mmol aryl iodide, 5.5 mmol acrylic acid or styrene or methyl acrylate, 3 mL DMF and 2.03 g Bu₃N were used. All products were identified by IR and H NMR. **Isolated yield based on aryl iodide.

The efficiency of the complexation method is illustrated by UV-Vis diffuse reflectance spectroscopy. **Figure 1** shows the UV-Vis adsorption spectra of organic silica ("Si"- NH_2) before and after Pd^{2+} or Cu^{2+} complexation in the range of 190-800 nm. It was found that there are two significant adsorption peaks at about 220 nm, 424 nm for " Si "- $\text{NH}_2 \cdot \text{Pd}^{2+}$ ", and 237 nm, 368 nm for " Si "- $\text{NH}_2 \cdot \text{Cu}^{2+}$ ", respectively. The peaks in the range of 190-800 nm in the UV-Vis spectrum after Pd^{2+} or Cu^{2+} complexation revealed that the charge transfer of $-\text{NH}_2$ and Pd^{2+} , Cu^{2+} occurred, the $-\text{NH}_2$ group did not show the adsorption in this range.

Figure 1 UV-Vis diffuse reflectance spectra of " Si "- $\text{NH}_2 \cdot \text{Pd}^{2+}$ or " Si "- $\text{NH}_2 \cdot \text{Cu}^{2+}$ catalysts



a, " Si "- NH_2 ; b, " Si "- $\text{NH}_2 \cdot \text{Pd}^{2+}$; c, " Si "- $\text{NH}_2 \cdot \text{Cu}^{2+}$

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