

Letter

# Silica-supported poly- $\gamma$ -aminopropylsilane $\text{Ni}^{2+}$ , $\text{Cu}^{2+}$ , $\text{Co}^{2+}$ complexes: efficient catalysts for Heck vinylation reaction

Yuanfa Yang<sup>a,b</sup>, Renxian Zhou<sup>a</sup>, Shaofen Zhao<sup>a</sup>, Qiaoling Li<sup>a</sup>, Xiaoming Zheng<sup>a,\*</sup>

<sup>a</sup> Institute of Catalysis, Zhejiang University, Hangzhou 310028, PR China

<sup>b</sup> Institute of Physical Chemistry, Zhejiang Normal University, Jinhua 321004, PR China

Received 13 March 2002; accepted 24 June 2002

## Abstract

Silica-supported poly- $\gamma$ -aminopropylsilane transition metal ( $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ) complexes have been prepared. These catalysts are highly active and stereoselective for Heck vinylation reaction of aryl iodide with olefins at 130–150 °C, and can be reused after washing without loss in activity. An induction period of more than 2 h was observed.

© 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Heck reaction; Poly- $\gamma$ -aminopropylsilane; Transition metal complex; Induction period

## 1. Introduction

The vinylation of aryl halides (Heck reaction), one of the most important C–C bond formation reactions in organic synthesis is mostly catalyzed by palladium complex in homogenous solution [1–4]. Recently, several publications have appeared on the development of heterogeneous catalysts [5,6], such as supported palladium on carbon [7], metal oxides [8] and zeolites [9], and silica-supported palladium complexes [10], in order to perform Heck vinylation reaction in a simple and inexpensive way. Comparison with supported palladium catalysts, supported transition metal (Cu, Co, Ni) catalysts are much less expensive for Heck reaction, but catalytic activity decreased rapidly [11] when it was reused. We report here the application of silica-supported poly- $\gamma$ -aminopropylsilane transition metal ( $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ) com-

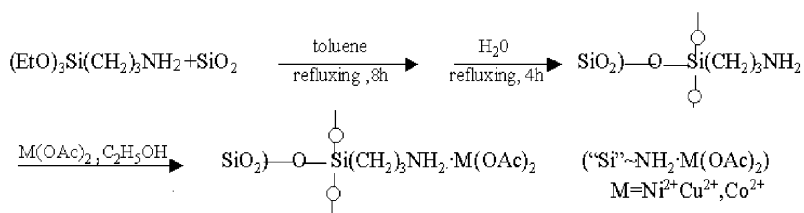
plexes for a C–C bond formation, viz. the Heck reaction. These catalysts give *trans*-products in high yields at 130–150 °C and can be reused after washing without loss in activity. In addition, an induction period of more than 2 h is found in the Heck reactions.

## 2. Experimental

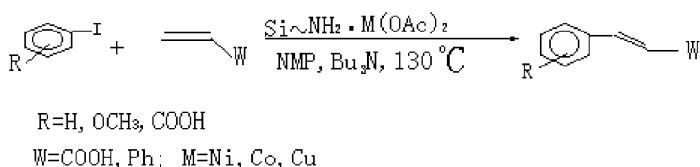
The supported transition metal complex catalysts (abbreviated as “Si”~NH<sub>2</sub>·M(OAc)<sub>2</sub>, M =  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Co}^{2+}$ ) could be easily prepared by the reaction of poly- $\gamma$ -aminopropylsilane with fumed silica, followed by treatment with metal acetate in ethanol (Scheme 1). The Ni, Cu and Co contents were 3.9, 3.6 and 3.7 wt.%, respectively, and nitrogen content was 3.6 wt.% in “Si”~NH<sub>2</sub>·M(OAc)<sub>2</sub> catalysts.

In the presence of these catalysts, the vinylation reactions of substituted aryl iodides with a varieties of olefins were carried out at 130–150 °C, and gave the corresponding *trans*-product in high yields. The

\* Corresponding author. Tel.: +86-571-88273272;  
fax: +86-571-88273283.  
E-mail address: cuihua@dial.zju.edu.cn (X. Zheng).



Scheme 1.



Scheme 2.

*trans*-selectivity was always near quantitative, and no *cis*-product was observed (Scheme 2).

A typical reaction, a mixture of tri-*n*-butylamine (11 mmol), acrylic acid (10 mmol), iodobenzene (5 mmol), 3 ml NMP and 0.05 g “Si”~NH<sub>2</sub>·Ni(OAc)<sub>2</sub> (0.034 mmol) was stirred under N<sub>2</sub> in an oil bath at

130 °C. The reaction progress was monitored by TCL. After the reaction, the catalyst “Si”~NH<sub>2</sub>·Ni(OAc)<sub>2</sub> was separated from the mixture by filtration. A dilute HCl (2% solution) was poured into the filtrate, and then the white precipitate was filtered, washed by water and recrystallized to get *trans*-cinnamic acid.

Table 1

Vinylation reaction of substituted aryl iodides with alkenes catalyzed by supported transition metal catalysts<sup>a</sup>

Aryl iodide	Alkenes	Yield <sup>b</sup> (%) (time, h)		
		“Si”~NH <sub>2</sub> ·Ni(OAc) <sub>2</sub>	“Si”~NH <sub>2</sub> ·Cu(OAc) <sub>2</sub>	“Si”~NH <sub>2</sub> ·Co(OAc) <sub>2</sub>
	COOH	88 (4)	95 (3)	95 (2)
	Ph	98 <sup>c</sup> (15)	40 <sup>c</sup> (48)	39 <sup>c</sup> (48)
	COOH	97 (6)	91 (7)	71 (24)
	Ph	96 (15)	92 <sup>c</sup> (24)	91 <sup>c</sup> (24)
	COOH	92 (24)	86 <sup>c</sup> (48)	88 <sup>c</sup> (48)
	Ph	89 <sup>c</sup> (48)	85 <sup>c</sup> (48)	85 <sup>c</sup> (48)

<sup>a</sup> Reaction condition: The ratio of catalyst (M):substituted aryl iodide:alkenes is 0.034:5:10 (mol, M = Ni, Cu, Co). All products were characterized by IR or <sup>1</sup>H NMR. Reaction temperature is 130 °C.

<sup>b</sup> Isolated yields.

<sup>c</sup> Reaction temperature is 150 °C (because the reaction are hard to carry out at 130 °C).

### 3. Results and discussion

All catalysts were treated with  $\text{KBH}_4/\text{C}_2\text{H}_5\text{OH}$  before they were used. This results in the vinylation reactions of substituted aryl iodides with a varieties of olefins were summarized in Table 1. From Table 1, it could be seen that the vinylation reaction using supported Ni complex as catalysts gave the substituted products in high yields (88–98%) at 130–150 °C. Using supported Co and Cu complexes, also gave good yields (71–95%) of the substituted products except the reaction of iodobenzene with styrene, in which stilbene was obtained in about 40% yields. The function groups on benzene ring have influence on the activity of aryl iodides markedly. Longer reaction time was required in the reaction of 4-iodobenzoic acid with alkenes, and no reaction was observed with 4-iodonitrobenzene catalyzed by these catalysts.

The activities of the supported transition metal ( $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ) complexes without treatment with  $\text{KBH}_4$  were tested for the vinylation of iodobenzene with acrylic acid and their recycling studies were also carried out. The results were listed in Table 2. From Table 2, it was found that these catalysts gave high yields in the first run, but all reaction had longer

Table 2

Stability of supported  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Co}^{2+}$  catalysts for the vinylation reaction<sup>a</sup>

Catalyst <sup>a</sup>	Yield <sup>b</sup> (%) (time, h)		
	First run	Second run	Third run
"Si"~NH <sub>2</sub> ·Ni(OAc) <sub>2</sub>	87 (6)	89 (4)	86 (6)
"Si"~NH <sub>2</sub> ·Cu(OAc) <sub>2</sub>	93 (9)	94 (3)	87 (5)
"Si"~NH <sub>2</sub> ·Co(OAc) <sub>2</sub>	93 (11)	97 (2)	83 (6)

<sup>a</sup> Reaction temperature was 130 °C.

<sup>b</sup> Isolated yields.

reaction time and were performed in 6–11 h. In the recycling experiments, two recycling were carried out with all the catalysts. It was interesting that the yields of *trans*-product increased about 1–4% in the second run while all reaction were performed only in 2–4 h. The similar results had also been reported in recycling test for supported Pd catalysts [12]. The much shorter reaction time in the second run indicated that there was an induction period in the first run. In order to test the induction period, the reaction progress was monitored by GC in the first run (as shown in Fig. 1). It was found that an induction period of more than 2 h was observed for these catalysts. In the induction period studies of the supported Pd catalysts [13,14], the

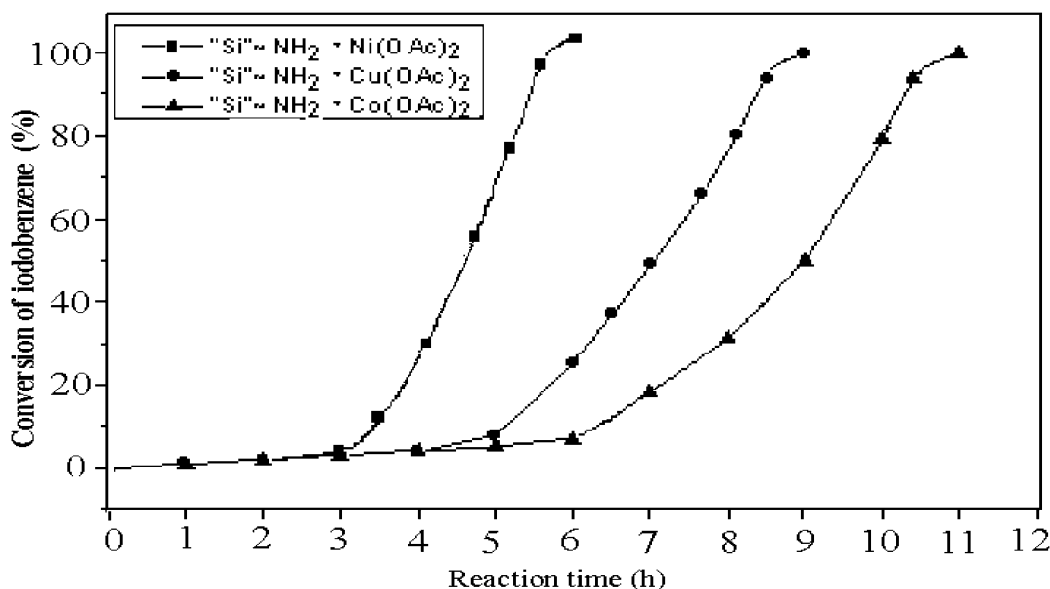


Fig. 1. The concentration of iodobenzene vs. reaction time for supported  $\text{M}^{2+}$  complexes.

authors thought that the induction period corresponded to the delay required for the reduction of precursor Pd<sup>2+</sup> species to the active Pd<sup>(0)</sup> and the reduction was probably caused by both styrene and OH groups in zeolite cages. Comparison of the results with Table 1 (entry 1) and Table 2 revealed that the supported M<sup>2+</sup> complexes treated with KBH<sub>4</sub>/C<sub>2</sub>H<sub>5</sub>OH exhibit similar catalytic properties to the catalysts used in second run. The XPS data of these catalysts (after the first run reaction) also revealed the presence of the metals of 0 and +1 oxidation state. The probable mechanism of the reaction should be similar to homogenous catalyst for the Heck reaction. Hence, we believed that the induction period observed in our experiments might be caused by the reduction of supported M<sup>2+</sup> species to the active M (0,1) (M = Ni, Cu and Co).

In conclusion, we have synthesized new catalysts for the vinylation Heck reaction—silica-supported transition metal Ni<sup>2+</sup>, Cu<sup>2+</sup>, Co<sup>2+</sup> complexes. These complexes exhibit a high activity and stereoselectivity at a lower reaction temperature of 130–150 °C, and can be reused after washing without loss in activity. It is interesting that an induction period of more than 2 h has been observed in the first run reactions for these catalysts.

## Acknowledgements

We thank the financial support of Nature Science Foundation of Zhejiang Province.

## References

- [1] H.A. Diech, R.F. Heck, *J. Am. Chem. Soc.* 96 (1974) 1133.
- [2] J.J. Bozell, C.E. Vogt, *J. Am. Chem. Soc.* 110 (1988) 2655.
- [3] T. Jeffery, *Tetrahedron Lett.* 40 (1999) 1673.
- [4] J.P. Genet, M. Savingnac, *J. Org. Chem.* 576 (1999) 305.
- [5] N. Shezad, A.S. Oakes, A.A. Clifford, C.M. Rayner, *Tetrahedron Lett.* 40 (1999) 2221.
- [6] B.M. Bhanage, F.-G. Zhao, M. Shinai, *Tetrahedron Lett.* 39 (1998) 9509.
- [7] M. Julia, M. Dutell, *Bull. Soc. Chim. Fr.* 9/10 (1973) 2790.
- [8] M. Wanger, K. Köher, L. Djakovitch, S. Weinkauff, V. Hagen, M. Muhler, *Top. Catal.* 13 (2000) 319.
- [9] L. Djakovitch, H. Heise, K. Köher, *J. Organomet. Chem.* 584 (1999) 16.
- [10] J.M. Zhou, R.X. Zhou, X.M. Zheng, *Chinese J. Chem.* 19 (2001) 987.
- [11] S. Iyer, V.V. Thakur, *J. Mol. Catal. Part A. Chem.* 157 (2000) 275.
- [12] K. Köher, M. Wanger, L. Djakovitch, *Catal. Today* 66 (2001) 105.
- [13] L. Djakovitch, K. Koehler, *J. Mol. Catal. Part A. Chem.* 142 (1999) 275.
- [14] M. Casey, J. Lawess, C. Shirran, *Polyhedron* 19 (2000) 517.