The vinylation of aryl iodides catalyzed by silica-supported poly-γ-aminopropylsilica Ni, Cu and Co complexes

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Silica-supported poly-γ-aminopropylsilica Ni, Cu and Co complexes were prepared from poly-γ-aminopropylsilane and fumed silica, followed by treatment with metal acetate in ethanol. These catalysts are highly active and stereoselective for vinylation of aryl iodides with olefins. They give a variety of *trans*-substituted products in high yields in both polar and non-polar solvents at 120–150 °C, and can be reused without loss in activity.

KEY WORDS: supported Ni, Cu and Co complexes; Heck reaction; vinylation.

1. Introduction

The vinylation of aryl halides (Heck reaction), one of the most important C–C coupling reactions in organic synthesis, is mostly catalyzed by palladium complexes in homogeneous solution [1–4], which have high activity and give excellent yields. However, homogenous catalysts are generally connected with problems of separation (purity of products), recovery and regeneration of the catalysts when applied to large-scale synthesis in industry. A solution to these problems consists in using supported catalysts [5–9], which can be easily separated by simple filtration and reused. Silica-supported poly-γ-aminopropylsilica palladium catalysts for the Heck reaction of iodides with olefins have been investigated in our laboratory [10]. They exhibit excellent activity and stereoselectivity. Here, we report on silica-supported poly-γ-aminopropylsilica Ni, Cu and Co catalysts for the vinylation of aryl iodides with olefins. These catalysts give good yields in both polar and non-polar solvents at 120–150 °C, and can be easily separated and reused without loss in activity. They exhibit much better catalytic properties than Ni/Al_2O_3, Cu/Al_2O_3, Co/Al_2O_3 and Ni/HY-zeolite catalysts [11] in recycling.

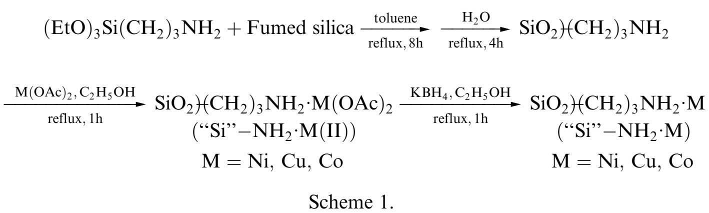
2. Experimental

2.1. Catalyst preparation

Silica-supported poly-γ-aminopropylsilica M(II) complexes (abbreviated as “Si”–NH_2·M(II), M = Ni, Cu and Co) were prepared by the reaction of poly-γ-aminopropylsilane with fumed silica, and then by treatment with the corresponding metal acetate in ethanol solution. The silica-supported M(II) complexes were treated with KBH_4 in ethanol solution again, to obtain silica-supported poly-γ-aminopropylsilica M complexes (abbreviated as “Si”–NH_2·M, M = Ni, Cu and Co) (scheme 1). The surface areas of the catalysts were about 60–70 m^2/g.

2.2. Measurements

The vinylations of aryl iodides with olefins were carried out at a temperature of 120–150 °C (scheme 2). A mixture of aryl iodide (5 mmol), olefin (10 mmol), tributylamine (11 mmol), solvent (3.0 ml) and catalyst (50 mg, 0.04 mmol metal) was stirred under N_2 in an oil bath for 2–48 h. The reactions were monitored by TCL or GC.



$$(EtO)_3Si(CH_2)_3NH_2 + \text{Fumed silica} \xrightarrow[\text{reflux, 8h}]{\text{toluene}} \xrightarrow[\text{reflux, 4h}]{H_2O} SiO_2)\!\!\!\!\text{(}(CH_2)_3NH_2$$

$$\xrightarrow[\text{reflux, 1h}]{M(OAc)_2,\,C_2H_5OH} \underset{\substack{(\text{“Si”}-NH_2\cdot M(II))\\ M\,=\,Ni,\,Cu,\,Co}}{SiO_2)\!\!\!\!\text{(}(CH_2)_3NH_2\cdot M(OAc)_2} \xrightarrow[\text{reflux, 1h}]{KBH_4,\,C_2H_5OH} \underset{\substack{(\text{“Si”}-NH_2\cdot M)\\ M\,=\,Ni,\,Cu,\,Co}}{SiO_2)\!\!\!\!\text{(}(CH_2)_3NH_2\cdot M}$$

Scheme 1.

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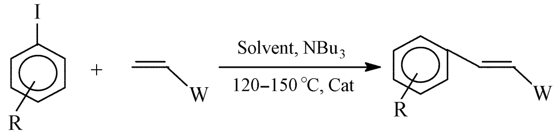


R = H, OCH_3, COOH
W = COOH, Ph, COOMe

Scheme 2

After reaction, the catalyst was separated from the mixture by filtration, and reused by washing with ethanol and drying in air. The filtrate was treated directly with 2% HCl solution to precipitate crude products, followed by recrystallization to give isolation yield.

Table 1
Comparison of "Si"–NH_2·M and "Si"–NH_2·M(II) catalysts[a]

Catalyst	Yield[b] (Time, h) (TOF[c], %)		
	120 °C	130 °C	140 °C
"Si"–NH_2·Ni(II)	97 (24) (5)	87 (6) (18)	91 (4) (28)
"Si"–NH_2·Cu(II)	94 (16) (7)	93 (9) (13)	95 (3) (40)
"Si"–NH_2·Co(II)	49 (48) (1)	93 (11) (11)	93 (7) (17)
"Si"–NH_2·Ni	90 (7) (16)	88 (4) (27)	92 (2) (58)
"Si"–NH_2·Cu	92 (8) (14)	95 (3) (40)	88 (2) (50)
"Si"–NH_2·Co	95 (5) (24)	96 (2) (60)	95 (2) (60)

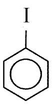
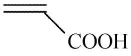
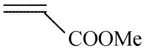
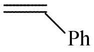
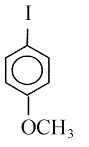
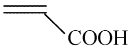
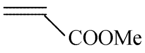
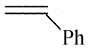
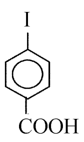
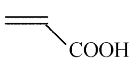
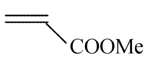
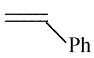
[a] Reaction conditions: catalyst (M) : iodobenzene : acrylic acid : NBu_3 = 0.04 : 5 : 10 : 11 (in mol). NMP was used as solvent.
[b] Isolation yields.
[c] TOF: mol product per mol M per h.

3. Results and discussion

3.1. *Activity of "Si"–NH_2·M and "Si"–NH_2·M(II) catalysts*

The activity of "Si"–NH_2·M and "Si"–NH_2·M(II) catalysts was investigated in the vinylation reaction of iodobenzene with acrylic acid at 120–150 °C. The results are shown in tables 1 and 2. As seen from table 1, there was a tendency for "Si"–NH_2·M(II) catalysts to take a longer time to complete the reaction (100% conversion of iodobenzene) than "Si"–NH_2·M catalysts. This was due to an induction period in the reaction catalyzed by "Si"–NH_2·M(II) catalysts. The induction period decreased with increasing reaction temperature. A similar induction period phenomenon occurring in the Heck reaction catalyzed by palladium-modified zeolites

Table 2
Vinylation reaction of substituted aryl iodides with olefins catalyzed by "Si"–NH_2·M catalysts[a]

Aryl iodide	Alkene	Yield[b] (Time, h) (TOF[c], %)		
		"Si"–NH_2·Ni	"Si"–NH_2·Cu	"Si"–NH_2·Co
 I	 COOH	89 (4) (28)	94 (3) (39)	96 (2) (60)
	 COOMe	90 (6) (19)	92 (7) (16)	94 (4) (29)
	 Ph	95[d] (15) (8)	40[d] (48) (1)	39[d] (48) (1)
 I, OCH_3	 COOH	96 (6) (20)	91 (7) (16)	71 (24) (4)
	 COOMe	92 (8) (14)	94 (7) (17)	95 (7) (16)
	 Ph	95 (15) (8)	92[d] (24) (5)	91[d] (24) (5)
 I, COOH	 COOH	92 (24) (5)	86 (48) (2)	88[d] (48) (2)
	 COOMe	86 (24) (4)	85[d] (48) (2)	79[d] (48) (2)
	 Ph	89[d] (48) (2)	85[d] (48) (2)	85[d] (48) (2)

[a] Reaction condition: catalyst (M) : aryl iodide : olefin : NBu_3 = 0.04 : 5 : 10 : 11 (in mol), 130 °C. NMP was used as solvent. All products were identified by IR or H^1 NMR.
[b] Isolation yields.
[c] TOF: mol product per mol M per h.
[d] Reaction temperature was 150 °C.

has been reported by Djakovitch and Koehler [12], and they suggested that the induction period corresponds to the reduction of the catalyst precursor Pd(II) species to the active Pd(0). Hence, we thought that the induction period in our experiments corresponds to the reduction of "Si"–NH_2·M(II) (M = Ni, Cu and Co) catalysts to low oxidation state M(0), which undergoes oxidative addition in the Heck vinylation reaction. This deduction agrees with the mechanism of the Heck reaction with aryl halides that the active species is a Pd(0) complex in palladium catalysts [13,14]. The reused catalysts (see table 4) exhibit the same activity as the "Si"–NH_2·M catalysts (see table 3), which also supported the opinion on the oxidation state change of supported M(II) complexes during the induction period. XPS data (252.8, 780.0 and 933.5 eV for "Si"–NH_2·Ni, "Si"–NH_2·Co and "Si"–NH_2·Cu, respectively) also showed that the "Si"–NH_2·M catalysts and reused catalysts had the same low oxidation state.

From table 2, it was found that the vinylation reaction of aryl iodides with olefins catalyzed by the "Si"–NH_2·M(II) catalysts gave the corresponding *trans*-product, the *trans*-selectivity was near quantitative and no *cis*-product was observed. Among these catalysts, the supported Ni complex exhibits the best catalytic properties because all the vinylation reactions except the reactions of iodobenzene and 4-iodobenzoic acid with stryene were carried out at 130 °C and produced good yields (86–96%). The functional groups on the benzene ring influenced the activity of aryl iodides markedly. 4-Iodoanisole and iodobenzene had higher activity than 4-iodobenzioc acid which required a longer time or higher temperature for completion of the reaction. Interestingly, these supported catalysts exhibit a similar activity to homogeneous catalysts in the Heck reaction, such as the $CoCl(pph_3)_3$ complex [15] and copper salts [16], which completed the reaction of 4-iodoanisole with methyl acrylate at 110 °C with 91% yield and at 150 °C with 85% yield, respectively; the $Ni[p(oph)_3]_4$ complex [17] completed the reaction of 4-iodoanisole with styrene at 150 °C with 95% yield.

Table 3
Effect of solvent on catalytic performance of "Si"–NH_2·M catalysts[a]

Solvent	Yield[b] (Time, h) (TOF[d], %)		
	"Si"–NH_2·Ni	"Si"–NH_2·Cu	"Si"–NH_2·Co
NMP	89 (4) (28)	94 (3) (39)	97 (2) (61)
HTP[c]	94 (5) (24)	94 (5.5) (21)	92 (6) (19)
o-Xylene	93 (5) (23)	93 (16) (7)	90 (24) (5)
n-Octyl alcohol	91 (3) (38)	91 (4) (28)	88 (5) (22)

[a] Reaction condition: catalyst (M) : iodobenzene : acrylic acid : NBu_3 = 0.04 : 5 : 10 : 11 (in mol), 130 °C.
[b] Isolation yields.
[c] Hexamethyl-phosphoric triamine.
[d] TOF: mol product per mol M per h.

Table 4
Recycling of "Si"–NH_2·M catalysts

Recycling	Solvent	Yield[b], %	Reaction time, h	TOF
Fresh	*n*-Octyl alcohol	90	7	16
1st cycle	*n*-Octyl alcohol	93	3	38
2nd cycle	*n*-Octyl alcohol	95	6	20
3rd cycle	*n*-Octyl alcohol	93	7	16
4th cycle	*n*-Octyl alcohol	94	6	20

[a] Reaction condition: catalyst (M) : iodobenzene : acrylic acid : NBu_3 = 0.04 : 5 : 10 : 11 (in mol), 130 °C.
[b] Isolation yields.

3.2. *Effect of solvent on catalytic performance*

The effect of solvent on catalytic performance was also investigated for the vinylation reaction of iodobenzene with acrylic acid catalyzed by the "Si"–NH_2·M catalysts at 130 °C. The results are shown in table 3. It was found that a polar solvent was good for the Heck reaction. Using the non-polar solvent *o*-xylene required a longer time for completion of the reaction.

3.3. *Recycling test*

The recycling capacity shown in table 4 for four recycles was consistent in the case of the supported Ni catalyst without any deactivation. It was found that the catalyst can be easily reused by simple filtration.

4. Conclusion

The heterogeneous "Si"–NH_2·M and "Si"–NH_2·M(II) (M = Ni, Cu and Co) catalysts exhibit excellent activity and stereoselectivity for the vinylation reaction of aryl iodides with olefins in both polar and non-polar solvents. An induction period was observed in the vinylation reaction catalyzed by supported M(II) catalysts. The induction period may correspond to the reduction of the catalyst precursor M(II) species to a low oxidation state (0) of Ni, Cu and Co. Recycling test showed the catalysts can be reused without loss of activity.

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