

Letter

The novel use of Ni, Co, Cu and Mn heterogeneous catalysts for the Heck reaction[☆]

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Abstract

Novel Ni, Co, Cu and Mn heterogeneous catalysts, catalyze the reaction of aryl and vinyl halides with olefins (Heck reaction) to give substitution products. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Heck reaction; Heterogeneous; Catalyst

The Pd catalyzed vinylation of aryl and vinyl halides has been extensively investigated by Heck and others [1–3] because of its wide application in organic synthesis. There are a few reports on the use of Nickel complexes for this reaction [4–7]. We have reported the use of Co, Rh, Ir, Cu and Ni (0) complexes for the same [8–10]. The use of Pd/C and other supported Pd catalysts for the Heck reaction has also been reported [11–13]. The use of Ni, Cu and Co heterogeneous catalysts for hydrogenation reactions is well known [14–16]. We report here the first application of these catalysts for a C–C bond formation reaction viz. the Heck reaction. The rationale behind the use of such catalysts was the low oxidation state (0 or 1) of the different metals in these catalysts and hence, the

possibility of their undergoing oxidative addition reactions.

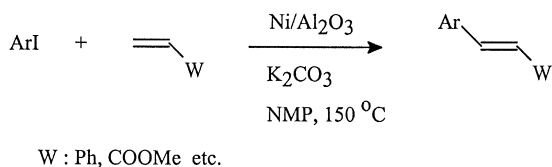
A number of supported and other heterogeneous catalysts, 20% Ni/HY-Zeolite, 20% Ni/Al₂O₃, 20% Co/Al₂O₃, 20% Cu/Al₂O₃, U–Ni–A, Co and Mn were prepared following literature procedures [14–17]. The vinylation of 4-MeO-iodobenzene with ethyl acrylate in the presence of these catalysts proceeded in high yields giving *trans*-ethyl cinnamate (Scheme 1). The result of these experiments is listed in Table 1. A number of aryl iodides and styryl bromide reacted with a variety of olefins in the presence of these catalysts, to give substitution products in moderate to high yields.

In a typical reaction, iodobenzene (0.234 g, 1 mmol), ethylacrylate (5 mmol), K₂CO₃ (0.276 g, 2 mmol), catalyst (0.025 g) and *N*-methylpyrrolidinone (5 ml) were taken in a round bottom flask and heated to 150°C. The reaction progress was monitored by TLC and most reactions were complete in 5–48 h. After comple-

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Scheme 1.

tion of reaction, the contents were poured into dil. HCl and extracted with ethyl acetate. Column chromatography gave the pure product in high yields.

In addition to the supported catalysts prepared, the Urushibara methodology was used for the preparation of heterogeneous catalyst from CoCl_2 , MnCl_2 and the Urushibara Ni catalyst from NiCl_2 . Typically, the Urushibara catalysts were prepared by the reduction of the corresponding metal halides with Zn dust. These catalysts were also found to be active for the Heck reaction. Comparison of the results with different catalysts and olefins revealed the supported Ni catalyst to be more reactive than the others. Vinyl acetate gave low yield of the substitution product. The Urushibara Ni catalyst gave only moderate yields of the substitution products. Reaction of styryl bromide with styrene and ethyl acrylate gave the substituted dienes in low yields (15–29%). With the Urushibara Co catalyst, all the olefins, except vinyl acetate gave the expected product, in moderate to low yields. In the reaction of iodobenzene with styrene catalyzed by $\text{Co/Al}_2\text{O}_3$, stilbene was obtained in 56% yield. Good yield of the substitution product was obtained in the reactions of other aryl iodides with ethyl acrylate catalyzed by $\text{Co/Al}_2\text{O}_3$. No reaction was observed with methyl methacrylate.

$\text{Cu/Al}_2\text{O}_3$ gave high yield of the substitution product even with methyl methacrylate. The Mn catalyst also gave moderate yields of the substituted products from the reaction of different olefins and aryl halides. Longer reaction time was required for methylmethacrylate, methacrolein and vinyl acetate. In addition, the yields were low, due to polymerization of these

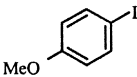
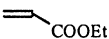
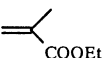

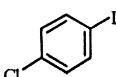
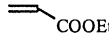
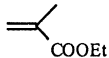

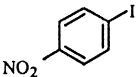
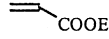
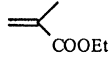

olefins under the harsh reaction conditions. None of these catalysts could activate aryl bromides or chlorides. Unlike the homogeneous catalysts, no addition of ligands was necessary for these heterogeneous catalyst mediated reactions. Reaction of 4-Cl-iodo-benzene with methylmethacrylate gave a mixture of the ester and carboxylic acid while 4-iodo-nitro-benzene gave 4-nitro-phenylmethyl methacrylate as the only product in the presence of Bu_3N as base.

Leaching and recycling studies were also carried out on these catalysts. In the leaching experiment, product formation (7–53% for the different catalysts) was observed, when the reactions were maintained at 150°C for 24 h. The leaching experiment was carried out as follows. The catalyst and rest of the reaction mixture, except the olefin, were maintained at 150°C for 24 h, followed by filtration to remove the catalyst and base. More base was added, followed by ethyl acrylate and the reaction mixture heated to 150°C for 24 h. Product formation was observed by TLC. This indicates that a considerable amount of the heterogeneous catalyst undergoes leaching under the reaction conditions.

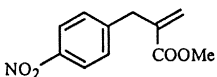
In the recycling experiment, three to four cycles were carried out with all the catalysts. Ni/HY-Zeolite , $\text{Ni/Al}_2\text{O}_3$, $\text{Cu/Al}_2\text{O}_3$ and U-Ni-A gave > 70% yield on the first recycle and above 40% yield on the second recycle. With Ni/HY-Zeolite catalyst, the second recycle also resulted in 73% yield. The third recycle gave 15–20% yield of the product with the rest of the starting material being recovered. U-Co-A , $\text{Co/Al}_2\text{O}_3$ and U-Mn-A gave only 15–33% yield of the product in the first recycle, 7–10% in the second and only traces of the product in the third recycle with recovery of the starting material. Traces of product were also observed in a blank reaction, where, only the alumina support (neutral Al_2O_3), was used without the catalyst.

The XPS data of these catalysts reveal the presence of the metals, in the 0 and +1 oxidation state. The probable mechanism of the reaction should be similar to the homogeneous cata-

Table 1
Heterogeneous catalysis (Ni, Cu, Co) of the Heck reaction

S. No.	Aryl Iodide	Olefin	Catalyst ^a Yield %			
			Ni/Al ₂ O ₃	Ni/HY-Zeolite	Cu/Al ₂ O ₃	Co/Al ₂ O ₃
1			94	95	88	85
			76	75	80	NR
			65	75	70	56
2			95	90	80	73
			9 (51) ^b	24 (25) ^b	22	28 (19) ^b
			85	58	71	73
3			95	90	34	23
			16 ^c	14 ^c	59 ^c	21 ^c
			60	68	66	50

a : All catalysts are 20% Metal/Support b : Yield in parenthesis is of the carboxylic acid

c : Bu₃N was used as base; Product 

All products were characterized by IR and ¹H NMR

lyst for the Heck reaction. We have thus shown the first use of a number of new heterogeneous catalysts for the Heck reaction. These catalysts can also be used for other such C–C bond formation reactions.

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