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 PII:
 S0022-328X(20)30256-4

 DOI:
 https://doi.org/10.1016/j.jorganchem.2020.121354

 Reference:
 JOM 121354

To appear in: Journal of Organometallic Chemistry

Received Date: 3 April 2020

Revised Date: 21 May 2020

Accepted Date: 25 May 2020

Please cite this article as: P.R. Sruthi, S. Anjali, N. Varghese, S. Anas, Novel and efficient polymer supported copper catalyst for heck reaction, *Journal of Organometallic Chemistry* (2020), doi: https://doi.org/10.1016/j.jorganchem.2020.121354.

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## Novel and Efficient Polymer Supported Copper Catalyst for Heck Reaction

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**Abstract:** A novel polymer supported copper complex (m-PAN-Cu) is prepared by immobilising Cuprous Iodide (CuI) on amidoxime modified Polyacrylonitrile (mPAN) and characterised by FTIR, XRD, EDX, ICP-MS and XPS analyses. This complex was further explored as a general and efficient heterogeneous catalyst for Heck coupling reaction of a series of aryl halides with olefins and afforded the corresponding coupling products in moderate to good yields. This catalyst offers easy preparation, good stability, excellent catalytic activity and reusability. This is the first study involving an amidoxime modified PAN supported copper catalyst towards greener and efficient Heck reaction.

Keywords: Green Chemistry, Heck Reaction, Heterogeneous Catalysis, Copper, Polymer Support

Mizoroki-Heck reaction is an important carbon-carbon bond forming reaction in organic synthesis and has been widely adopted as a key step towards the preparation of many complex organic molecules.<sup>1</sup> Classical Heck reaction involves the palladium catalyzed coupling between an alkene and aryl halide under homogenous reaction conditions.<sup>2</sup> The search for novel catalytic systems involving other transition metals such as Ni,<sup>3</sup> Co,<sup>4</sup> Rh,<sup>5</sup> Ir<sup>6</sup> and Cu<sup>7</sup> have also been received much attention in recent years for substituting palladium catalysts. Among which, easily available copper based catalytic systems are of special importance due to their cheaper price, functional group tolerance and scalability for large scale procedures. However, only limited

reports are available on the copper catalyzed Heck type reaction and are usually performed under increased catalyst loading, high temperature and longer reaction time. The copper catalyzed Heck type reaction of aryl and vinyl iodides with olefins was first reported by Iyer and coworkers in 1997, using a CuI/K<sub>2</sub>CO<sub>3</sub>/NMP catalyst system.<sup>7a</sup> After that, several catalytic approaches under CuI/DABCO,<sup>7b</sup> copper bronze/Ionic Liquid,<sup>7c</sup> microwave<sup>7d</sup> and ligand free<sup>7e</sup> conditions were developed for homogeneous copper catalyzed Heck type coupling reactions. However, homogeneous catalytic processes usually suffer from difficulties such as poor recyclability and reusability of the catalyst, possibility of metal contamination in the final products etc. Thus, heterogenization of homogeneous catalytic processes have emerged as an alternative to overcome these limitations.<sup>8</sup> Naturally, some interesting and useful heterogeneous palladium based catalytic systems were developed for Heck reaction<sup>9</sup> while corresponding copper catalyzed approaches are rare.<sup>10</sup> Therefore the development of mild and efficient heterogeneous copper catalytic systems for Heck coupling reaction remains as highly demanding and challenging area of research.

Immobilization of homogeneous catalysts into insoluble polymeric supports by covalent bonding or complexation/chelation enables the easy recovery and reuse of catalysts. In this context, the applicability of synthetically modified Polyacrylonitrile (PAN) polymers<sup>11</sup> in heterogeneous catalysis as efficient support for various transition metal catalyzed coupling reactions has been less investigated.<sup>12</sup> Utilization of a preoxidated PAN supported copper catalyst (Cu/Pre PAN fiber mat) for Heck coupling reaction was described by Shao et al.<sup>13</sup> Recently our group has disclosed the amidoxime modified PAN supported Palladium (II) complexes as efficient heterogeneous catalyst for Heck coupling reaction.<sup>14</sup> In light of this report as well as due to the lack of a general and efficient heterogeneous copper catalyzed methodology, we have now developed a novel polymer supported copper catalyst for Heck

coupling reaction by immobilizing the metal salt on amidoxime modified PAN. The details of the preparation, characterization of the supported copper complex and its catalytic activity, stability and reusability studies for Heck type coupling reactions are presented.



Scheme 1. Synthesis of the polymer supported Cu catalyst

The preparation of the supported copper complex (m-PAN-Cu) through a two-step procedure is illustrated in scheme 1. First step involves the synthetic modification of nitrile group in PAN 1 leading to poly acrylamidoxime 2 on reaction with hydroxyl amine hydrochloride. Next step is chelation of CuI with 2 in acetonitrile to form the supported copper complex 3 (m-PAN-Cu). The formation and structure of 3 was characterized using various spectroscopic techniques.

The synthetic modification of PAN and subsequent metal complexation was initially evidenced from FTIR analyses and further studied by X-ray diffraction (XRD) analyses. Fig 1 gives the FTIR spectra of PAN, m-PAN and m-PAN-Cu. It is found that after modification reaction, the intense peak due to CN group at 2245 cm<sup>-1</sup> (**Fig 1a**) was disappeared and the characteristic bands of amidoxime groups corresponding to OH/NH, C=N, C-N, N-O stretching vibrations were observed at 3100 to 3300, 1646, 1389, and 918 cm<sup>1</sup> respectively (**Fig 1b**). In the case of m-PAN-Cu, the absorption bands of N-O, C=N vibrations became less intense and shifted to lower frequency, accompanied with a weakening of OH/NH stretching (**Fig 1c**), implying the complexation of copper salt with amidoxime groups. As shown in figure 2a, the reflection planes of (100) at  $2\Theta = 17.02$  and (020) at  $2\Theta = 28.88$  were readily recognized from the XRD pattern of PAN indicating partial crystalline nature. However, the XRD pattern of the m-PAN exhibited amorphous characteristics after modification (**Fig. 2b**). But in the case of m-PAN exhibited amorphous characteristics after modification (**Fig. 2b**).

PAN-Cu (**Fig. 2c**) three diffraction peaks at  $2\Theta$ = 25.02, 42.10 and 49.90 are attributed to the (111), (220) and (311) planes indicating the presence of crystalline Cu(I) phase.



Figure 1 and 2: FTIR (left) and XRD (right) Spectra of (a) PAN, (b) m-PAN, (c) m-PAN Cu



Figure 3: EDX spectrum of m-PAN-Cu complex

Energy-Dispersive X-ray spectroscopy (EDX) analysis confirmed the presence of 10.32 wt% of copper in m-PAN-Cu along with other expected elements like carbon, nitrogen, oxygen, and iodine (**Figure 3**). Notably, the EDX results did not reveal any significant contamination from other metal ions or from unwanted sources. Further, the ICP-MS analysis of the m-PAN-Cu complex **3** provided the copper content in the complex as 0.0094 g per 1g. Moreover, XPS studies were carried out to analyze the exact oxidation state of constituent elements and the spectra is shown in **figure 4**. The less intense binding energy peaks of copper observed at 935.23 eV and 951.97 eV corresponding to Cu 2p3/2 and 2p1/2 respectively indicated the presence of copper (I) species. The binding energy values of C1s, N1s, and O1s were detected at 286.88,

401.65 and 533.21 eV respectively. These observations in comparison with the literature values<sup>13</sup> clearly revealed the presence of Cu(I) species, coordinated to the amidoxime group in the complex.



Figure 4: (a) XPS data of m-PAN-Cu complex (b) High resolution analysis of  $Cu_{2P}$  signal

After detailed characterization of the m-PAN-Cu, next we have investigated the catalytic efficiency of this complex in promoting the Heck coupling reaction. Initial trail with 1 eq. of iodo benzene (**4a**) and 1.2 eq. of methyl acrylate (**5a**) in presence of 2 mol% of m-PAN-Cu catalyst, 3 eq. NaHCO<sub>3</sub> base and NMP (2 mL) solvent at 140 °C for 24h under nitrogen atmosphere gave the corresponding coupling product (**6a**) in 51 % isolated yield (Scheme 2).

Scheme 2. Heck reaction using m-PAN-Cu catalyst

To probe the influence of various reaction parameters, the effect of catalyst loading, bases, temperature and solvents on promoting the reaction was screened under the reaction condition and the results are summarized in table 1. Firstly, the amount of catalyst was screened; and when loading increased to 3 mol%, the yield was increased to 66% (Table 1, entry 1). Further increase in catalyst loading (5 mol%) did not influenced much, while significant lowering in reaction

yield was resulted when catalyst loading was decreased to 1 mol% (Table 1, entry 2). Therefore 3% of catalyst was used for further studies. Other reaction parameters such as base and solvent were optimized through a series of experiments (Table 1, entry 3-10). A considerable increase in the reaction yield upto 81% was resulted by using  $K_2CO_3$  as the base (Table 1, entry 3).  $Cs_2CO_3$  failed to deliver the product (Table 1, entry 4), while organic base DABCO gave only 33% yield (Table 1, Entry 5). Interestingly, use of Et<sub>3</sub>N as base provided **6a** in 78% yield (Table 1, Entry 6). Later, various solvents including N-methylpyrrolidone (NMP), DMF, DMSO, Dioxane and H<sub>2</sub>O were explored by using K<sub>2</sub>CO<sub>3</sub> as base (Table 1, Entry 7-10) and none of the solvent gave better result than NMP.

Entry	Base	Solvent	Yield (%) <sup>b</sup>
1	NaHCO <sub>3</sub>	NMP	66(67) <sup>c</sup>
2	NaHCO <sub>3</sub>	NMP	33 <sup>d</sup>
3	K <sub>2</sub> CO <sub>3</sub>	NMP	82
4	Cs <sub>2</sub> CO <sub>3</sub>	NMP	trace
5	DABCO	NMP	33
6	Et <sub>3</sub> N	NMP	78
7	$K_2CO_3$	DMF	25
8	$K_2CO_3$	DMSO	32
9	$K_2CO_3$	Dioxane	38
10	$K_2CO_3$	H <sub>2</sub> O	nd
11	$K_2CO_3$	NMP	nd <sup>e</sup>
12	$K_2CO_3$	NMP	43 <sup>f</sup>
13	$K_2CO_3$	NMP	$80^{ m g}$

Table 1: Optimization studies

<sup>a</sup>Reaction conditions: **4a** (1 eq.), **5a** (1.2 eq.), Base (3 eq.), solvent (2 ml), m-PAN-Cu (3 mol %), N<sub>2</sub> atm, 140 °C, 24 h,

<sup>b</sup>Isolated yield, <sup>c</sup>5 mol% catalyst, <sup>d</sup>1mol% catalyst, <sup>e</sup>without catalyst or Base, <sup>f</sup>at 120 °C, <sup>g</sup>36h reaction

When control experiments were performed in the absence of catalyst or base no product formation was observed (Table 1, Entry 11). This hinted that the presence of catalyst and base are essential for promoting this reaction, under the given conditions. Finally, the effect of temperature and reaction time were investigated. When the reaction was performed at lower temperature (120 °C), only 43% product formation was observed (Table 1, Entry 12) and longer reaction time did not provide much improved results (Table 1, Entry 13).

Based on these initial screening studies an optimized reaction condition was established for the Heck coupling reaction using m-PAN-Cu catalyst. Under this optimized reaction conditions, we then examined a series of substrate scope studies to evaluate the generality of this methodology and the results are summarized in Table 2. It was interesting to observe that the m-PAN-Cu complex is capable of catalyzing Heck coupling reaction between a number of substituted aromatic halides and olefins. When bromo benzene 4b and chloro benzene 4c are treated with methyl acrylate 5a under the optimized reaction condition, product 6a was isolated only in 36 % and 15% yields respectively (Table 2, entry 2-3). While, Iodo benzene 4a showed good reactivity with other activated alkenes such as ethylacrylate 5b, tertiary butylacrylate 5c, acrylic acid 5d, acrylamide 5e and styrene 5f and afforded the corresponding coupling products in moderate to good yields (Table 2, entry 4-8). Similarly, functionalized aryl iodides containing both electron withdrawing and electron donating groups underwent efficient coupling reaction with alkenes. For example, aryl iodides with Nitro, Methoxy and Methyl substitution at para positions(4d-f) reacted well with methylacrylate 5a, to yield the corresponding products (6g-i) in moderate to good yields (entry 9,10 and 11). Relatively low reaction yields were observed, when Iodo anisole 4d and 4-Iodonitrobenzene 4e were subjected to coupling with styrene 5f (entry 12 and 13). While, reaction of 2-iodo toluene 4g with methylacrylate 5a resulted in lower product

yield (34%, entry 14). Notably, in all the cases, complete *trans* selectivity was observed and the formations of *cis* or homo coupling products were not observed.

		¥ ⊥ ∠	<u>m-PA</u>	N-Cu (3 mol%		$R_2$	
	R <sub>1</sub>		R <sub>2</sub> K <sub>2</sub> C	$CO_3$ (3 equiv), (2  ml) 140°C	• R <sub>1</sub>		
	4:	a-g	5a-f	24h, N <sub>2</sub>	, 6a-l		
Sl.		Aryl Ha	lide	Al	kene	Droduct	Yield
No	X	$\mathbf{R}_1$		$\mathbf{R}_2$		TTouuct	(%) <sup>a</sup>
1	Ι	Н	<b>4</b> a	CO <sub>2</sub> Me	5a	<b>6</b> a	82
2	Br	Н	<b>4</b> b	CO <sub>2</sub> Me	5a	6a	36
3	Cl	Н	<b>4</b> c	CO <sub>2</sub> Me	5a	6a	15
4	Ι	Н	<b>4</b> a	CO <sub>2</sub> Et	5b	6b	73
5	Ι	Н	<b>4</b> a	$\mathrm{CO}_2^{t}\mathrm{Bu}$	5c	6c	64
6	Ι	Н	4a	CO <sub>2</sub> H	5d	6d	52
7	Ι	Н	<b>4</b> a	CONH <sub>2</sub>	5e	6e	57
8	Ι	Н	4a	Ph	5f	6f	45
9	Ι	4-OMe	4d	CO <sub>2</sub> Me	5a	6g	61
10	Ι	4-NO <sub>2</sub>	<b>4e</b>	CO <sub>2</sub> Me	5a	6h	82
11	Ι	4-Me	<b>4f</b>	CO <sub>2</sub> Me	5a	6i	46
12	Ι	4-OMe	<b>4d</b>	Ph	5f	6j	44
13	Ι	$4-NO_2$	<b>4</b> e	Ph	5f	6k	23
14	Ι	2-Me	4g	CO <sub>2</sub> Me	5a	61	34

Table 2: Substrate scope studies

<sup>a</sup>Isolated yield

Finally, the recyclability and reusability of the m-PAN-Cu catalyst was tested for coupling reaction between **4a** and **5a** under the optimized conditions. After completion of the reaction, the catalyst **3** was recovered from the reaction mixture by simple filtration and washed with ethylacetate. Then the recovered catalyst was directly used for the next cycle of reaction, without any additional treatment. This process was repeated upto 5 cycles and observed that the catalyst exhibits reasonably good activity even after recycling. These results are tabulated in Table 3.

able 5. Reusu	Juliy	sinuie	s usin	g m-1	<i>AN-</i> (
Run	1	2	3	4	5
%Yield <sup>[a]</sup>	82	80	76	69	63
<sup>[a]</sup> Isolated vield					

 Table 3. Reusability studies using m-PAN-Cu

The information about the mechanism of Heck reaction under heterogeneous catalysis is very limited. Earlier studies have evidenced that the actual active species in supported Heck catalysis (especially with palladium), are the soluble metal species leached out from the starting solid material and partially or completely re-precipitated onto the support at the end of the reaction.<sup>12, 15a</sup> In a similar manner, a possible mechanism for the Heck reaction using the supported copper catalyst is presented in Scheme 3. The catalytic cycle begin with the dissolution of the active metal species Cu(I)<sub>Solv</sub> **A** from the support at higher temperature, which then undergoes oxidative addition with aryl iodide **4a** in solution to form intermediate **B**. This step follows the migratory insertion of the **B** into the olefin via  $\pi$ -complexation leading to the formation of intermediate complex **C**. The product **6a** is formed from this complex **C** by the  $\beta$ H elimination and the active the copper (I) complex is regenerated from H-Cu-I by the removal of HI which is quenched by the base.<sup>7b, 15b</sup>



Scheme 3. Plausible reaction mechanism

In conclusion, we have developed a novel, stable and efficient polymer supported copper catalyst for Heck coupling reaction of a series of substrates. The catalyst can be easily prepared by chelating Cuprous Iodide (CuI) with amidoxime modified Polyacrylonitrile (PAN). Detailed characterization of the catalyst was done using FTIR, XRD, EDX and XPS analyses, which clearly indicated the formation of the polymer copper complex (m-PAN-Cu). This m-PAN-Cu complex (**3**) was further explored as an effective heterogeneous catalyst for Heck coupling reaction. The catalytic activity of **3** has been verified over a series of substrates and the corresponding coupling products were isolated in moderate to good yields. This studies revealed that the anchoring of the Copper salt on the modified polymeric support not only exhibits improved catalytic activity, stability and product selectivity but also enables easy preparation, recovery and reusability of the catalyst at least for 5 cycles. To the best of our knowledge this is the first report of using amidoxime modified PAN supported copper catalyst for Heck type coupling reaction. Therefore, despite of its low reactivity, the developed catalyst offers the prospect for being an excellent greener alternative to conventional homogeneous catalytic systems for Heck reaction.

PRS thank the Council of Scientific and Industrial Research (CSIR), New Delhi for Junior Research Fellowship (Grant No. 09/499(0088)/2015-EMR-1). NV thanks Kerala State Council for Science, Technology and Environment (KSCSTE) for Student Project Scheme (No. 739/SPS63/2018/KSCSTE). Authors are thankful to St. Thomas College (Pala), SAIF (CUSAT), IIRBS and School of Environmental Sciences, Mahatma Gandhi University for Spectroscopic Analyses. Authors also thank DST-PURSE. Govt. of India (SR/417 and 418/2017) for the financial assistance.

## **Conflicts of interest**

There are no conflicts to declare

## **References and Notes**

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## Highlights

- A novel Copper complex (m-PAN-Cu) is prepared by immobilizing CuI on amidoxime modified Polyacrylonitrile (PAN) and characterized.
- m-PAN-Cu is explored as an efficient and greener heterogeneous catalyst for Heck • reaction.
- First report of Heck reaction using a copper catalyst immobilized on amidoxime • functionalized PAN.
- This catalyst offers easy preparation, good stability, excellent catalytic activity and • reusability.

stability,

## **Declaration of interests**

 $\boxtimes$  The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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