**N-Heterocyclic Carbene-Palladium Complex on Polystyrene Resin Surface as Polymer-Supported Catalyst and Its Application in Suzuki Cross-Coupling Reaction**

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**Abstract:** A poly(imidazoliummethyl styrene)-surface grafted-polystyrene resin was prepared by suspension polymerization. This was used as the polymer-supported carbene precursor for the palladium complex, which efficiently catalyzed the Suzuki cross-coupling of aryl halides and phenylboronic acid.

**Keywords:** polymer-supported $N$-heterocyclic carbene (NHC), heterogeneous catalysis, palladium (Pd), Suzuki cross-coupling, imidazolium, suspension polymerization

Since $N$-heterocyclic carbenes were first introduced by Öfele and Wanzlick\(^1\), they have become universal ligands in organometallic and inorganic coordination chemistry. They exhibit a similar $\sigma$-donor and low $\pi$-acceptor ability as phosphine. Moreover, these NHCs have an excellent air and moisture stability, and have higher dissociation energies than other ligands, which have been quantified by theoretical calculations for different metals.\(^2\) Therefore, they can efficiently bind to any transition metal in the low or high oxidation states.

Many successful demonstrations of homogeneous catalysis using the NHCs as a ligand for transition metals, particularly palladium,\(^3\) have been reported. However, there are several problems with these homogeneous catalysis systems. These include the separation and recycling of the catalysts and contamination of the ligand residue in the final product. In order to avoid these problems, several types of heterogeneous catalysts have recently been developed by anchoring the Pd-adppp onto a PS-PEG\(^4\), and a Pd-NHCs complex onto a Wang resin\(^4\) and PS-DVB\(^6\). Recently, we also synthesized Pd-NHCs onto a Merrifield resin and demonstrated their excellent catalytic activity.\(^4\) However, these polymer-supported catalysts have catalytic active sites in all the regions of the resin, including the interior, making it difficult for reagents to diffuse into the interior of the resin, thereby reducing the overall reaction rate. All chemical reactions can proceed more effectively if the catalytic active sites are located at the resin surface.\(^5\)

This paper reports a method for preparing a novel polymer-support containing 1-methyl-3-(4-vinylbenzyl) imidazolium hexafluorophosphate group, $[\text{MVBIM}][\text{PF}_6]$, on the surface of the resin and demonstrate its efficacy as a polymer-supported NHC ligand for a Pd-catalyst in Suzuki cross-coupling in the aqueous

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phase. In order to prepare this support, a suspension polymerization system of styrene, DVB and a synthetic ionic liquid co-monomer with a vinyl group, which is immiscible with styrene and water, was used.

As shown in Scheme 1, the ionic liquid monomer, [MVBIM][PF$_6$].(2) was readily synthesized. This ionic liquid monomer (2) was not only insoluble in the aqueous phase but also in the styrene phase. Therefore, this ionic liquid monomer (2) could be located at the interface between the aqueous phase and organic phase in the suspension polymerization system.

![Chemical structure](image)

**Scheme 1.** Synthesis of the polymerizable ionic liquid monomer (2), [MVBIM][PF$_6$].

Poly(imidazoliummethyl styrene)-sg-polystyrene (PS) resin, where sg denotes surface grafted, was prepared by utilizing a conventional suspension polymerization system with a reactor and an overhead stirrer. The synthetic ionic liquid monomer (3.0, 5.0 and 7.0 g) was suspended in an aqueous phase, which consisted of water (150 ml) and PVA (0.75 g). An organic phase consisted of styrene (7.0 ml), DVB (0.7 ml, 50% in ethylvinylbenzene) and benzoyl peroxide (0.22 g), as an initiator. As shown in Figure 1, all the resins are the bead type (diameter of 38~150 μm) with imidazolium group loading levels of 0.23~1.12 mmol/g, which could be adjusted by changing the amount of the ionic liquid monomer. The CLSM (Confocal Laser Scanning Microscope) image of the fluorescent dye, 5(6)-carboxytetramethyl rhodamine, -adsorbed resins showed that all of the imidazolium groups were located on the surface of the resins.

![SEM micrograph](image)

**Figure 1.** (a) SEM micrograph of the poly(imidazoliummethyl styrene)-sg-PS resin.
(b) CLSM image of the 5(6)-carboxytetramethyl rhodamine-adsorbed resin.

In order to apply this poly(imidazoliummethyl styrene)-sg-PS resin to the reactions in the aqueous phase,$^6$ the swelling property in water and various organic solvents was measured. The difference in the swelling...
volume between the hydrophobic and hydrophilic solvents was quite low, which means that the new resin is amphiphilic compared to conventional polystyrene-based resins, and can be used in all the solvents, even in water.

The poly(imidazoliummethyl styrene)-sg-PS resin (0.23 mmol/g) was used as a NHC ligand precursor for the Pd-catalyzed Suzuki cross-coupling. In order to form the complexes between the palladium and the imidazolium groups, a mixture of Pd(OAc)$_2$ and the resins was shaken in DMF/H$_2$O for 2 h at 50°C with Cs$_2$CO$_3$, which played a role as a base for the deprotonation of the imidazolium groups. The loading levels of the immobilized palladium were measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The amount of Pd(OAc)$_2$ was varied to determine the optimal loading of immobilized palladium. It was observed that almost all of the imidazolium groups (0.23 mmol/g) on the resins participated in the formation of the Pd-NHC complex (0.11 mmol-Pd/g) when a 4-fold excess of Pd(OAc)$_2$ was used.

The catalytic activity of the polymer-supported Pd-NHC complexes with a palladium loading of 0.11 mmol/g was investigated for the Pd-catalyzed Suzuki cross-coupling of the aryl halides with phenylboronic acid. The coupling of iodosobenzene (0.5 mmol) and phenylboronic acid (0.6 mmol), as a model reaction, was performed using the polymer-supported Pd-NHC complexes (1.1 mol.%) in an aqueous solution of Na$_2$CO$_3$ (2.5 mmol). Several reaction variables, such as reaction time and solvents, were examined and the results are summarized in Table 1.

**Table 1.** Suzuki cross-coupling of Ph-I with Ph-B(OH)$_2$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Temp.</th>
<th>Time</th>
<th>Yield (%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Water</td>
<td>50°C</td>
<td>3 hr</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>Water</td>
<td>50°C</td>
<td>12 hr</td>
<td>36</td>
</tr>
<tr>
<td>3</td>
<td>Water / DMF</td>
<td>50°C</td>
<td>1 hr</td>
<td>93</td>
</tr>
<tr>
<td>4</td>
<td>Water / DMF</td>
<td>50°C</td>
<td>12 hr</td>
<td>96</td>
</tr>
<tr>
<td>5$^c$</td>
<td>Water / DMF</td>
<td>50°C</td>
<td>1 hr</td>
<td>83</td>
</tr>
<tr>
<td>6$^d$</td>
<td>Water / DMF</td>
<td>50°C</td>
<td>1 hr</td>
<td>81</td>
</tr>
</tbody>
</table>

$^b$ Assessed by HPLC analysis.
* All of the reactions were carried out with the mole ratio of Ph-I: Ph-B(OH)$_2$: Na$_2$CO$_3$: Pd = 1: 1.2: 5.0: 0.01. The imidazolium loading capacity of starting polymeric support was 0.23 mmol/g.

* Isolation yields were calculated from the mass of the biphenyl product after separation by column chromatography.

* The repeat experiment with the polymeric support catalyst of entry 3 under the same conditions. (the 2nd use)

* The repeat experiment with the polymeric support catalyst of entry 5 under the same conditions. (the 3rd use)

In summary, a polymer-supported Pd-NHC complex, which is located on the surface of the resin beads, was prepared using a simple procedure. It was confirmed that the Pd-NHC complexes on the polymeric support catalyzed the Suzuki cross-coupling reaction quite effectively in the water/DMF phase with satisfactory yields and excellent purities. A more efficient polymer system for the Pd-NHC complex and its catalytic activity in the cross-coupling reactions are currently under investigation.

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References


