Immobilization of Palladium Acetate on Ionic Liquid Copolymerized Polystyrene: A Way to Eliminate Inhibiting Effect of Imidazolium Chloride and Enhance Catalytic Performance

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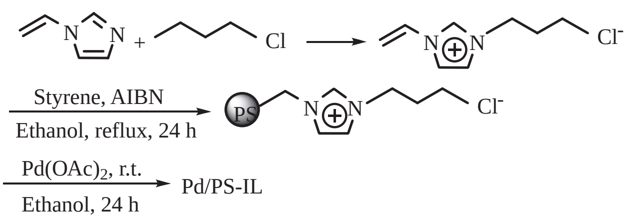
Immobilization of palladium acetate on a novel polymeric support that is prepared by copolymerization of 3-butyl-1-vinylimidazolium chloride with styrene is demonstrated to be an effective way to eliminate inhibiting effect of imidazolium chloride and enhance catalytic performance.

Over the past few years, ionic liquids have gained an increasing reorganization as a kind of novel and versatile solvents for synthetic chemistry. One of the most attractive applications of ionic liquids is that they can be used as reaction medium for a variety of transition-metal-catalyzed reactions.[1] In most cases, replacing common organic solvent with ionic liquid can result in a number of improvements in terms of product separation, reaction rate enhancement, and catalyst recycling.[1]

A few examples of palladium-catalyzed alkoxycarbonylation and hydrogenation reactions in the presence of ionic liquids have been reported, which revealed that the components of ionic liquids played an important role in both reactions.[2–8] $PdCl_2(PPh)_3$ or $Pd(OAc)_2$ catalyzed methoxycarbonylation of styrene could afford medium to high yields of products in 1-methylimidazolium-based ionic liquids consisted of anions such as BF_4^-, PF_6^-, or NTf_2^-. Interestingly, however, Cl^- as anion has been observed to bear a strong inhibiting effect towards this reaction.[2] When $[BMIm]BF_4$ or $[BMIm]NTf_2$ were used as reaction solvent, for example, yields of products were 53 and 60%, respectively, but yet a addition of 0.5 wt % [BMIm]Cl in $[BMIm]NTf_2$ would lead to a nearly 40% decrease of products yield, and only a 3% yield of products was obtained in pure [HMIm]Cl.[4] Similar inhibiting effect of imidazolium chloride was also observed in the case of palladium-catalyzed methoxycarbonylation of iodobenzene.[3,6] It had been proposed that the formation of palladium carbene complex between imidazolium chloride and $Pd(OAc)_2$ is the major reason that lead to this inhibiting effect.[6] Moreover, Cl^- is also known for its negative effect for transition-metal-catalyzed hydrogenation reaction performed in ionic liquid.[9]

In this paper, we report the preparation of a kind of novel copolymer by copolymerization of styrene with [BVIm]Cl (3-butyl-1-vinylimidazolium chloride), which was denoted as PS-IL, and its use as solid support to immobilize transition-metal. Immobilization of $Pd(OAc)_2$ on PS-IL was demonstrated to be an effective way to eliminate the inhibiting effect mentioned above. Supported Pd catalyst so formed can give high catalytic performances, even much better than its IL-free homogeneous counterpart, for both alkoxycarbonylation and hydrogenation reactions.

Preparations of PS-IL supported palladium catalyst, denoted as Pd/PS-IL, were showed in Scheme 1. In order to get a better understanding of the behavior of PS-IL as solid support, another two kinds of supported Pd catalysts were also prepared. One, denoted as Pd/PS, was prepared by immobilization of $Pd(OAc)_2$ on polystyrene that was synthesized using the same way as that of PS-IL. Another one, Pd/SiO_2-IL, was prepared following a similar route reported previously, where $Pd(OAc)_2$ was fixed on the surface of imidazolium chloride pretreated silica gel.[10]

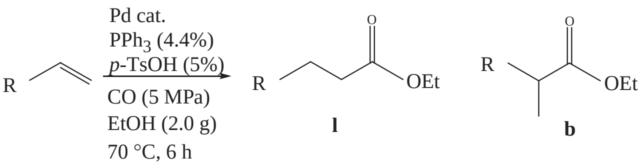


Scheme 1. Preparations of PS-IL.

The details of experiments regarding catalysts preparations, characterizations as well as their catalytic uses for alkoxycarbonylation and hydrogenation reactions can be found in the supporting information.

Then ethoxycarbonylation reactions of styrene were carried out in the presence of different Pd catalysts, and the results were summarized in Table 1. As can be seen, this reaction can be smoothly carried out using $Pd(OAc)_2$ as homogeneous catalyst (Run 1). However, when $Pd(OAc)_2$–[BVIm]Cl system was used,

Table 1. Alkoxycarbonylation reactions catalyzed by Pd catalyst[a]



Run	Substrate	Cat.	Yield/%[b]	**l/b**
1[c]	Styrene	$Pd(OAc)_2$	50	1.76
2[c]	Styrene	$Pd(OAc)_2$–[BVIm]Cl	—	—
3[c]	Styrene	$Pd(OAc)_2$–[BDMIm]Cl	89	1.5
4[c]	Styrene	Pd/SiO_2-IL	—	—
5[c]	Styrene	Pd/PS-IL	81	1.08
6[c]	Styrene	Pd/PS	21	1.18
7[d]	*p*-CS[e]	Pd/PS-IL	42	1.2
8[d]	1-Hexene	Pd/PS-IL	98	3
9[d]	IB[f]	Pd/PS-IL	38	—

[a]Substrate: 1.0 g. [b]GC yield. [c]Styrene/Pd: 880. [d]Substrate/Pd: 6000. [e]*p*-CS: *p*-chlorostyrene. [f]IB: iodobenzene, 20% NEt_3 was also used and the product was ethyl benzoate.

no occurrence of reaction was observed (Run 2). Replacing [BVIm]Cl with its C-2-substituted analogue [BDMIm]Cl (3-butyl-1,2-dimethylimidazolium chloride), on the contrary, can result in a 89% products yield under the same reaction condition (Run 3), which strongly suggested that the formation of palladium carbene complex at the C-2 position of imidazolium cation was the reason that lead to the observed inhibiting effect. Pd/SiO_2-IL behaved in a similar way to that of $Pd(OAc)_2$–[BVIm]Cl system (Run 4), suffering a failure for ethoxycarbonylation of styrene, which could also be attributed to the same reason—the formation of palladium carbene complex on the surface of silica gel (Run 4). Unexpectedly, a 80% product yield was achieved over Pd/PS-IL, which was even much better than that of homogeneous $Pd(OAc)_2$ (Run 5). Pd/PS, the polymer supported analogue of Pd/PS-IL, afforded a yield of products as 21% (Run 6).

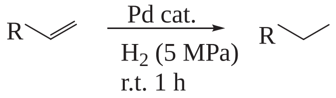
Based on the above results, especially the differences in activities of Pd/PS-IL, Pd/SiO_2-IL, and Pd/PS-Il, it could be safe to say that PS-IL as solid support played a crucial role to eliminate the inhibiting effect. As the formation of palladium carbene complex was the causation of the inhibiting effect, we were inclined to think that the observed elimination of the inhibiting effect by PS-IL was possibly derived from its ability to block out the formation of palladium carbene complex, most likely from the steric hindrance of benzyl group of styrene, as which was near to C-2 position of imidazolium cation.

ICP analysis revealed a very small Pd leaching of Pd/PS-IL, only 0.071 wt % Pd was detected in the post-reaction solution, implying Pd was stably fixed on PS-IL. On the contrary, it was very hard for Pd to be immobilized on polystyrene, as Pd black precipitate could be observed after reaction when Pd/PS was used as catalyst, which also implied that in this case ethoxycarbonylation of styrene underwent in a homogeneous way.

Pd/PS-IL was also active for ethoxycarbonylation of other substrates such as *p*-chlorostyrene, 1-hexene, and iodobenzene (Runs 7 to 9). Medium to high yields of product could be obtained in all of these cases.

Pd/PS-IL was also high active catalyst for hydrogenation reaction. As can be seen from Table 2, when different Pd catalysts were used for hydrogenation of 1-hexene, Pd/PS-IL exhibited the best catalytic performance. Keeping the ratio of 1-hexene to Pd as 24,000, a 82.2% yield of product could be attained over Pd/PS-IL after 1 h reaction at room temperature under 5 MPa H_2 (Run 3), which was much better than that of homogeneous $Pd(OAc)_2$ (21%, Run 1), biphasic $Pd(OAc)_2$–[BVIm]Cl (10%, Run 2), heterogeneous analogues Pd/SiO_2-IL (8.9%, Run 4) and Pd/PS (55%, Run 5). This remarkable improvement of Pd/PS-IL in terms of reaction rate may be attributed to the enhancement of the interfacial area between catalyst–substrate, one of the well-known benefits of polymer-supported catalyst system.[11] On the other hand, the lower activities of both $Pd(OAc)_2$–[BVIm]Cl and Pd/SiO_2-IL than that of $Pd(OAc)_2$ could also be reasonably explained by the formation of palladium carbene complex, as which was found to be less easy reducible under reduction condition.[6] Pd/PS-IL was also reusable catalyst for hydrogenation of 1-hexene. For example, it can be reused for 3 times no significant loss of activity (Run 6). In the case of hydrogenation of 1-hexene, no loss of Pd was detected by ICP analysis. Pd/PS-IL was also active catalyst for hydrogenation of other substrates such as, 1-octene, 1-decene, and cyclohexene (Runs 7 to 9). It should be noted that better results could be obtained over linear substrates.

Table 2. Hydrogenation of alkene catalyzed by different Pd catalyst[a]



Run	Substrate	Cat.	Alkene/Pd	Yield /%[c]
1	1-Hexene	$Pd(OAc)_2$	24000	21
2	1-Hexene	$Pd(OAc)_2$-[BVIm]Cl	24000	10
3	1-Hexene	Pd/PS-IL	24000	82
4	1-Hexene	Pd/SiO_2-IL	24000	8.9
5	1-Hexene	Pd/PS	24000	55
6	1-Hexene	Pd/PS-IL	12000	100 (98)[b]
7	Cyclohexene	Pd/PS-IL	6000	65
8	1-Octene	Pd/PS-IL	12000	82
9	1-Decene	Pd/PS-IL	12000	80

[a]Substrate: 0.027 mol. [b]3rd reuse of Pd/PS-IL. [c]GC yield.

In conclusion, we demonstrated herein the feasibility of employing styrene–ionic liquid copolymer as a kind of novel polymeric support to immobilize transition-metal. Based on the catalytic performances of supported Pd catalyst so formed in alkoxycarbonylation and hydrogenation reactions, we believe this method has potential applications in synthetic chemistry.

References and Notes

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