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Semi-hydrogenation of alkynes using phosphinated polymer incarcerated (PI) palladium catalysts

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Received 5th December 2005, Accepted 20th January 2006
First published as an Advance Article on the web 6th February 2006
DOI: 10.1039/b517181d

Phosphinated polymer incarcerated (PI) palladium catalysts prepared from a palladium(0) complex and phosphinated styrene-based polymers were found to show good selectivity in semi-hydrogenation of alkynes without strict control of H_2 consumption. Moreover, these catalysts could be removed by simple filtration and without any leaching of Pd.

Semi-hydrogenation[1] of alkynes to (*Z*)-alkenes is an important process not only in the laboratory but also in industry. However, the control of the selectivity between semi-hydrogenation and over-hydrogenation is a difficult issue. The Lindlar catalyst [Pd on $CaCO_3$ poisoned by $Pb(OAc)_2$, $PbSO_4$ or $BaSO_4$] is probably the most widely applied heterogeneous catalyst[2] for this transformation, although other heterogeneous[3] and homogeneous catalysts[4,5] have been developed. In several cases, very high semi-hydrogenation selectivity has been achieved (>99%) by controlling the H_2 gas consumption.[5a] However, higher chemoselectivity, reproducibility, generality and recyclability of the catalysts are still desired.

Recently, we reported the immobilization of palladium clusters into phosphinated polystyrene-based copolymers using the polymer incarcerated (PI) method.[6,7] These heterogeneous phosphinated PI Pd catalysts are highly active for carbon–carbon bond-forming reactions such as the Suzuki–Miyaura coupling even without the addition of any external phosphine ligands.[6f] Moreover, these catalysts may be recovered quantitatively by simple filtration and reused several times without loss of activity. The phosphine moiety of the polymer supports is assumed to have two main roles: suppression of the leaching of palladium, and enhancement of the catalytic activity as ligands. We also considered the possibility that the phosphines in the polymer support might act as a poisoning agent of the metal[8] realizing both chemoselective hydrogenation and suppression of metal leaching. In this paper, we describe the chemoselective semi-hydrogenation of alkynes using phosphinated PI Pd catalysts prepared from polymer supports possessing diphenylphosphino groups as potential poisoning agents of palladium.

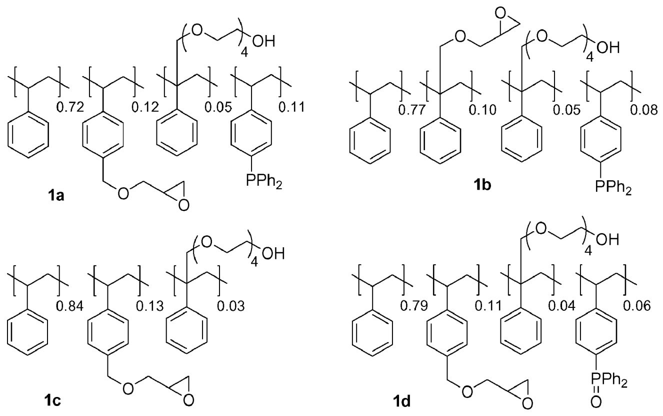
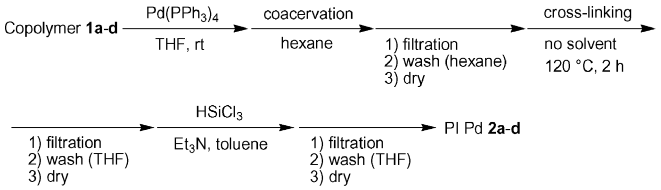


Fig. 1 Structures of polymer supports.



	loading of Pd (mmol/g)	ratio of P/Pd
PI Pd **2a**	0.36	2.1
PI Pd **2b**	0.32	1.8
PI Pd **2c**	0.67	0
PI Pd **2d**	0.38	2.9

Scheme 1 Preparation of phosphinated PI Pd catalysts.

First, phosphinated PI Pd **2a** and **2b** were prepared from copolymers **1a** and **1b** (Fig. 1) in the presence of $Pd(PPh_3)_4$ according to the PI method (Scheme 1). Since some phosphines were oxidized to the corresponding phosphine oxides during the preparation of the catalyst, the catalysts were treated with $HSiCl_3/Et_3N$[9] after cross-linking to give phosphinated PI Pd **2a** and **2b**. It was established by ^{31}P SR-MAS NMR analysis[10] that the phosphine oxides on the copolymer were completely reduced to the corresponding phosphines.[11] Transmission electron microscopic (TEM) analysis showed that small Pd clusters were dispersed on the polymer support without the formation of large Pd clusters and that the size of the Pd clusters was smaller than 1.5 nm. For the purposes of comparison, non-phosphinated PI Pd **2c** and phosphine oxide-containing PI Pd **2d** were prepared from copolymers **1c** and **1d** without $HSiCl_3$ reduction, respectively.

We then applied PI Pd **2a**–**2d** to the hydrogenation of diphenylacetylene (Table 1). In the cases of PI Pd **2c** and **2d** having no phosphine, fast hydrogenations were observed and saturated hydrogenated products were obtained quantitatively (entries 3 and 4). On the other hand, phosphinated PI Pd **2a** and **2b** gave semi-hydrogenated products **4** selectively under the same reaction conditions without the need for control of H_2 gas consumption and the addition of external poisoning agents (entries 1 and 2). Leaching of the palladium was examined by fluorescence X-ray (XRF) analysis after removal of the catalyst, and no leaching was detected in all cases. These results indicate that phosphine

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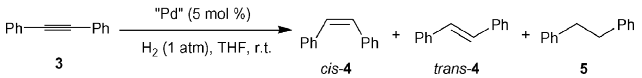
Table 1 Hydrogenation of diphenylacetylene using phosphinated PI Pd **2a**–**2d**

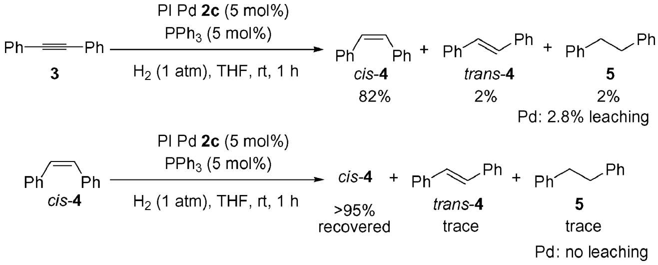


Entry	Catalyst (P/Pd)[a]	Reaction time/h	Recovery of **3** (%)	Yield (%)[b] *cis*-**4**	*trans*-**4**	**5**	Pd leaching (%)[c]
1	PI Pd **2a** (2.1)	1	0	59	5	32	nd
2	PI Pd **2b** (1.8)	1	14	69	6	17	nd
3	PI Pd **2c** (0)	1	0	0	0	100	nd
4	PI Pd **2d** (2.9)	1	0	0	0	100	nd

[a] The ratio of the diphenylphosphino groups in the polymer to the Pd atoms. [b] Yield was determined by ^1H NMR analysis using durene as an internal standard. [c] Determined by XRF analysis, nd = not detected (<0.94%).

moieties can act as moderate poisoning agents of Pd playing the same role as $PbSO_4$ or $BaSO_4$ in the Lindlar catalyst systems. In general, the poisoning of palladium by phosphines is too strong because phosphorus atoms of phosphines coordinate to palladium atoms strongly, and adsorption of hydrogen molecules and substrates is suppressed by the steric bulkiness and electronic effect of phosphines.[8a] Therefore, hydrogenation doesn't proceed in the presence of phosphines in homogenous catalytic systems. In the case of phosphinated PI Pd catalytic systems, however, diphenylphosphino groups in the polymer support might act as 'weak' poisoning agents because coordination of the phosphines to the palladium atoms is restricted by the steric bulkiness of the polymer supports.

In order to confirm the effect of phosphines as poisoning agents, a combination of non-phosphinated PI Pd **2c** and externally added PPh_3 was tested (Scheme 2). Diphenylacetylene (**3**) was hydrogenated to give *cis*- and *trans*-stilbene (**4**) in good yields with high selectivity, while the hydrogenation of *cis*-stilbene (**4**) was almost completely suppressed. These results indicate that PPh_3, which should be a very strong poisoning agent in homogeneous Pd systems, acted as a 'weak' poisoning agent within the sterically restricted polymer supports. However, 2.8% of palladium was leached from the polymer support into the solvent by the addition of PPh_3. Therefore, it is better to introduce phosphine moieties on polymer supports like PI Pd **2a** or **2b** rather than to add external phosphines.



Scheme 2 Effect of PPh_3 on the catalysis of PI Pd **2c**.

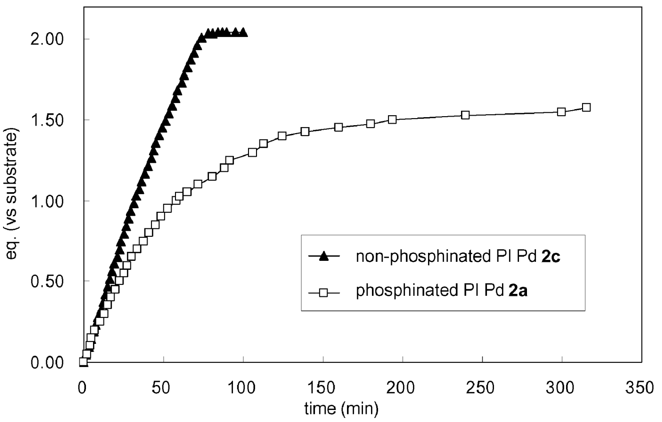


Fig. 2 H_2 consumption in the hydrogenation of diphenylacetylene using phosphinated PI Pd **2a** *vs.* non-phosphinated PI Pd **2c**.

Monitoring the H_2 consumption showed that the consumption rate with phosphinated PI Pd **2a** was slower than that with non-phosphinated PI Pd **2c**, and became even slower after about 1.5 equivalents of H_2 were consumed (Fig. 2). The reaction profile of the product distribution also demonstrated that diphenylacetylene was converted rapidly and that the proportion of *cis*-stilbene reached the maximum around after 60 min (Fig. 3). Although *cis*-stilbene was slowly over-hydrogenated to 1,2-diphenylethane, there was little appreciable change in the product distribution after 150 min. These results indicate that the over-hydrogenation step is much slower than the first semi-hydrogenation step, because the catalytic activity is suppressed by the 'weak' co-ordination of phosphines to the Pd clusters in the polymer support.

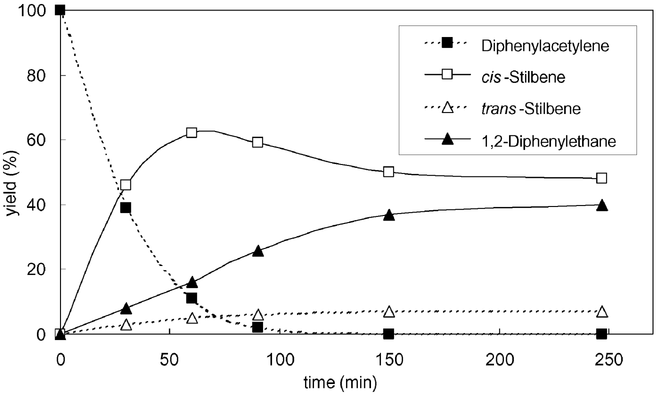
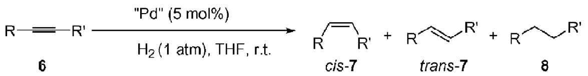
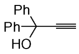
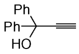
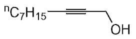
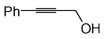


Fig. 3 Reaction profile of the hydrogenation of diphenylacetylene using PI Pd **2a**.

Table 2 Phosphinated PI Pd-catalyzed semi-hydrogenation of several types of alkynes



Entry	6	Catalyst	Reaction time/min	Recovery of 6 (%)	Yield (%)[a] cis-7	trans-7	8	Pd leaching (%)[b]
1	$Ph-C\equiv C-CO_2Et$	PI Pd **2a**	60	7	58	7	22	nd
2	$MeO_2C-C\equiv C-CO_2Me$	PI Pd **2a**	30	5	75	Trace	13	nd
3		PI Pd **2a**	30	0	82		15	nd
4		PI Pd **2c**	30	0	90		10	nd
5		PI Pd **2a**	20	20	74	Trace	Trace	nd
6		PI Pd **2a**	20	11	74	Trace	9	nd

[a] Yield was determined by ^{1}H NMR analysis using durene as an internal standard. [b] Determined by XRF analysis, nd = not detected (<0.94%).

For comparison, the Lindlar catalyst (Pd–$CaCO_3$ poisoned with Pb)[12] was tested under the same reaction conditions. Although the Lindlar catalyst showed a higher selectivity of the semi-hydrogenation of diphenylacetylene than the phosphinated PI Pd catalyst (Fig. 4), over-hydrogenation to 1,2-diphenylethane was remarkably observed after all conversion of the alkyne. Therefore, in the case of the Lindlar catalyst, exact control of H_2 consumption and/or other additives such as quinoline is necessary to obtain semi-hydrogenated products with high selectivity.

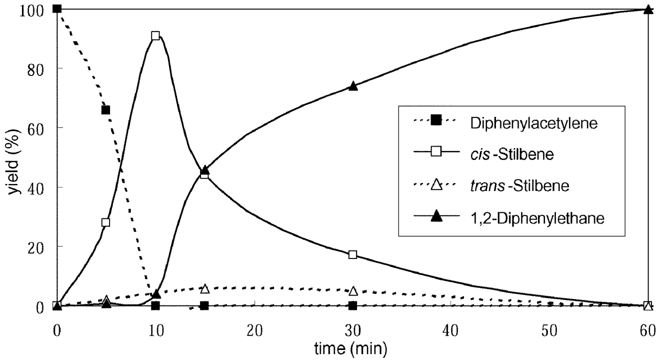


Fig. 4 Reaction profile of the hydrogenation of diphenylacetylene using Pd–$CaCO_3$ poisoned with Pb.

We applied phosphinated PI Pd **2a** and **2b** to the semi-hydrogenation of several types of alkynes (Table 2). Alkynes having aromatic, aliphatic, hydroxy, and/or alkoxycarbonyl groups provided the corresponding semi-hydrogenated products in good yields without any leaching of palladium. In these hydrogenations, small amounts of *trans*-alkene products were obtained.[4i,13] We confirmed that these *trans*-products were formed by the Pd-catalyzed isomerization of *cis*-products.

In summary, we have demonstrated that phosphinated PI Pd served as an effective catalyst for the selective semi-hydrogenation of alkynes without the addition of poisoning agents and without strict control of H_2 consumption. These heterogeneous catalysts can be prepared by simple methods and recovered by simple filtration. It is believed that the phosphine moieties act as appropriately weak poisoning agents due to the steric effect of the polymer supports. Further studies will focus on the effect of the phosphinated polymer supports on the catalytic activity of the metals.

This work was partially supported by Grant-in-Aid for Scientific Research from the Japan Society of the Promotion of Sciences (JSPS).

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