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RESEARCH NOTE

Recyclable Homogeneous/Heterogeneous Catalytic Systems for Heck Reaction through Reversible Transfer of Palladium Species between Solvent and Support

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The reversible transfer of Pd species between solvent and support occurs for Heck reactions of iodobenzene with methyl acrylate in *N*-methylpyrrolidone (NMP) using triethylamine and sodium carbonate as bases. When a homogeneous Pd catalyst was used with an additional support, the Pd species deposited on the support after the completion of reaction. Then Pd was easily separated from the reaction mixture, and it was successfully used for repeated reactions, which were mainly catalyzed by Pd species dissolved in solution. The transfer of Pd strongly depends on the surface nature of support materials and the reaction conditions used. © 2000 Academic Press

Key Words: **palladium catalyst; Heck reaction; phase transfer; recyclable catalyst.**

Heck reactions are an important tool for various organic syntheses involving the formation of carbon–carbon bonds (1–5). Organometallic complex catalysts are active for Heck reactions as well as other various organic syntheses (1–7). The reactions are mostly conducted homogeneously in solvents in which the catalysts, reactants, and products are soluble. For practical application, the reaction systems should be heterogeneous to make easy the separation and recycling of the catalysts. Although several types of heterogenized Heck catalysts using organopalladium complexes have been developed (7), conventional supported palldium catalysts can still rival those catalysts in practical usefulness. Several authors previously studied Heck reactions in organic solvents using supported palladium catalysts (8–13).

When supported palladium catalysts are used for Heck reactions, some palladium atoms are leached out into solvents and the dissolved palladium is mainly active species (9, 11, 12). Recently, we have studied the leaching (dissolution) of supported palladium into solvent during Heck vinylation reactions of iodobenzene (12). It is interesting that the quantity of dissolved palladium is decreased when the reaction is completed; almost all the dissolved palladium species can redeposit on the support, and they can be recycled without loss of activity. The present work has been undertaken to study the details of this mass transfer between solvent and support by using homogeneous or heterogeneous catalysts in the absence or presence of additional palladium-free support materials. The palladium can exist in solution, on the support, or in the form of free colloidal particles, and the transfer between these phases depends on the surface nature of the supports and the reaction conditions used.

Two supported catalysts, 10% Pd/C and 1% Pd/SiO_2, were used; the former was a commercial catalyst (Wako Pure Chem.), and the latter was prepared by ion exchange using $Pd(NH_3)_4Cl_2$ and a silica gel (Aldrich Chem. Co., Davisil grade 646). These Pd/C and Pd/SiO_2 catalysts were reduced by flowing hydrogen at 250 and 450°C, respectively, for 3 h. A few palladium compounds (Table 4) were used as homogeneous catalysts without ligands. The materials given in Table 1 were used as additional Pd-free supports along with the heterogeneous and homogeneous catalysts. Heck reactions of iodobenzene with methyl acrylate in NMP with triethylamine and sodium carbonate were carried out in a 100-mL autoclave under ambient conditions in the same manner used previously for homogeneous (12, 14) and heterogeneous (12, 15) reactions. The reaction conditions used are indicated in the following (Tables 2–4). The reaction mixture was analyzed by FID-GC. Only a Heck coupling product (only a single peak) was seen on GC charts under the reaction conditions used; that is, methyl cinnamate was produced in 100% selectivity. The conversion was determined from the amount of iodobenzene consumed, and error limits for the percentage off conversion data were less

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TABLE 1

BET Surface Areas and Sizes of Supports Used

Support	Surface area ($m^2\ g^{-1}$)	Size
Carbon (1)[a]	1354	<50 μm
Carbon (2)[b]	1293	0.14–0.20 mm
Silica gel[c]	300	0.25–0.45 mm
Silica gel heat-treated[d]	307	0.25–0.45 mm

[a] Activated charcoal, powder, Wako Pure Chem. Ind.

[b] Activated carbon, 80–100 mesh, Nihon Chromato Ind.

[c] Silica gel, 35–60 mesh, Aldrich Chem. Co., Davisil grade 646.

[d] The above silica gel was treated in air at 500°C for 4 h.

than ±3.0% due to the reproducibility of the data for repeated runs. The amount of Pd in solution was measured by atomic absorption spectrometry (AAS), and that of Pd on support was also determined by AAS after the extraction of Pd with aqua regia. The separation of solid materials for Pd/C and SiO_2 and for C and Pd/SiO_2 was easy to do by size after filtration following reaction. Although a small quantity of carbon powder was possibly mixed with silica granules, cross-contamination was much less significant, judging from the weights of the silica granules before and after reaction. The surface properties of supports were characterized by FTIR, and the existence of Pd on supports and free colloidal Pd particles was examined by scanning electron microscopy–X-ray microanalysis (SEM–XMA).

The Heck reaction was carried out with a supported Pd catalyst in the presence of an additional support, and the results obtained are shown in Table 2. In these cases, the reaction mainly proceeded homogeneously with Pd species dissolved from support into solvent (12). All the Pd species redeposited onto the support after the completion of reaction (100% conversion of iodobenzene), and no free Pd particles were observed. For the Pd/C catalyst, the Pd redeposition occurred onto the original support, carbon; for Pd/SiO_2, in contrast, about 2/3 of the original quantity of Pd transferred onto another added support, C(1). Namely, in the latter case, the dissolved Pd species deposited more favorably onto C(1) than onto the original SiO_2 support.

Table 3 shows the results on Heck reactions with a homogeneous catalyst, $Pd(NH_3)_4Cl_2$, in the presence of additional support materials. For C(1), all Pd species were present on its surface after the reaction was completed; for C(2), however, about 10% of Pd still remained in solution. The Pd species are more difficult to transfer from solvent onto C(2) than onto C(1), so more Pd species are in solvent, resulting in a larger rate of reaction for the former. Compared with the carbon supports, SiO_2 supports did not facilitate the deposition of Pd from solvent onto them. For heat-treated SiO_2, the Pd was little detected by SEM–XMA but free colloidal Pd particles were observed to form. There are no differences in the surface area between the two carbon supports and between the two SiO_2 supports, as shown in Table 1. Then, the chemical nature of those materials should be important, and FTIR results are shown in Fig. 1. The spectra in the range 1700–1000 cm^{-1} for C supports are significantly different before and after Heck reaction. There are marked differences in the absorption peaks at 1600 and 1200 cm^{-1} assigned to $\nu_{C=C}$ of aromatic rings and to $\nu_{C\text{–}O}$ of phenol, ether, and carboxyl groups, respectively (16–18). The intensities of these absorption bands are weak for the C(2) support and become weaker for both C(1) and C(2) after reaction. These surface functional groups may facilitate the deposition of Pd species from NMP solvent. Figure 1b shows FTIR results in the range of surface hydroxyl groups for SiO_2 supports (19, 20), their absorption intensity decreasing after reaction and heat-treatment. So, the surface hydroxyl groups may be important for the transfer of Pd between solvent and SiO_2 support. The difference between C and SiO_2 supports would be ascribable to the surface area in addition to the surface chemistry. The Pd deposition is also likely to occur on residual Pd particles on supports. Further work is needed, however, to elucidate the detailed mechanism of Pd deposition.

Three Pd precursors were used for the Heck reaction with and without an additional support of C(1). Table 4 shows

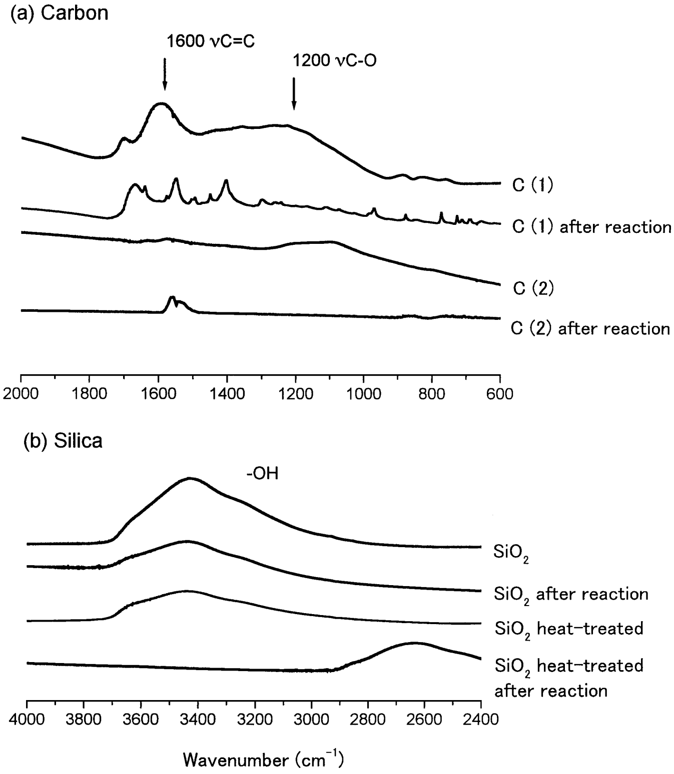

FIG. 1. FTIR spectra for carbon and silica supports: C(1), C(2), SiO_2, and heat-treated SiO_2 before and after Heck reaction.

TABLE 2

Results on Heck Reactions of Iodobenzene with Methyl Acrylate by Supported Pd Catalysts in the Presence of Additional Supports

Catalyst	Additional support	Time (h)	Conversion (%)	Pd distribution[a] on: Original support (%)	Pd distribution[a] on: Additional support (%)	Free Pd particles
10% Pd/C	SiO_2	1	100	99	1	not observed
1% Pd/SiO_2	C(1)	1	100	33	66	not observed

Note. Reaction conditions: iodobenzene and methyl acrylate, 5 mmol each; sodium carbonate, 2.5 mmol; triethylamine, 2 mmol; solvent NMP, 30 ml; catalyst, 80 mg for 10% Pd/C (Pd 0.0752 mmol) and 150 mg for 1% Pd/SiO_2 (Pd 0.0141 mmol); additional support, SiO_2 and C(1) 50 mg each. The reactions were carried out at 100°C for 30 min and then at 160°C for 30 min.

[a] The amounts of Pd on the original and additional supports were measured by AAS after the extraction with aqua regia.

TABLE 3

Results on Homogeneous Heck Reactions of Iodobenzene with Methyl Acrylate in the Presence of Supports

Catalyst	Support	Time (min)	Conversion (%)	Pd distribution[a]: In solution (%)	Pd distribution[a]: On support (%)	Free Pd particle
$Pd(NH_3)_4Cl_2$	C(1)	5	45	21	79	no
		60	100	0	100	no
$Pd(NH_3)_4Cl_2$	C(2)	5	72	86	14	no
		60	100	11	89	no
$Pd(NH_3)_4Cl_2$	SiO_2	5	99	93	7	no
		60	100	37	63	no
$Pd(NH_3)_4Cl_2$	treated SiO_2	5	100	38	nd[b]	observed
		60	100	0	nd[a]	observed

Note. Reaction conditions: iodobenzene and methyl acrylate, 5 mmol each; sodium carbonate, 2.5 mmol; triethylamine, 2 mmol; solvent NMP, 30 ml; catalyst, 3.4 mg (Pd 0.014 mmol); support 150 mg; temperature, 160°C; time, 60 min.

[a] The concentrations of Pd in solution were measured by AAS, and the residual amounts of Pd were assumed to be on the support.

[b] Palladium was not detected by SEM/X-ray microanalysis.

TABLE 4

Results on Homogeneous Heck Reactions of Iodobenzene with Methyl Acrylate in the Absence and Presence of Support

Catalyst	Support	Time (min)	Conversion[a] (%)	Pd distribution[a,b]: In solution (%)	Pd distribution[a,b]: On support (%)	Free Pd particle
$Pd(NH_3)_4Cl_2$		5	100 (10, 2)	31 (10, 8)	—	observed
		30	98 (78, 8)	4 (37, 8)	—	observed
		60	98 (100, 12)	0 (0, 8)	—	observed
$PdCl_2$		5	100	31	—	observed
		60	98	0	—	observed
$Pd(OAc)_2$		5	82	10	—	observed
		60	100	0	—	observed
$Pd(NH_3)_4Cl_2$	C(1)	5	45 (43, 47)	21 (17, 17)	79 (83, 83)	no
		60	100 (100, 100)	0 (0, 0)	100 (100, 100)	no
$PdCl_2$	C(1)	5	100 (11, 10)	15 (20, 11)	85 (80, 89)	no
		60	98 (98, 100)	0 (0, 0)	100 (100, 100)	no
$Pd(OAc)_2$	C(1)	5	85 (15, 15)	64 (13, 10)	36 (87, 90)	no
		60	98 (100, 100)	0 (0, 0)	100 (100, 100)	no

Note. Reaction conditions: iodobenzene and methyl acrylate, 5 mmol each; sodium carbonate, 2.5 mmol; triethylamine, 2 mmol; solvent NMP, 30 ml; catalyst, 0.014 mmol; support, 150 mg; temperature, 160°C; time, 60 min.

[a] First and second figures in parentheses indicate the data of the first and second recyclings, respectively.

[b] With respective to the initial quantity of Pd loaded. The concentrations of Pd in solution were measured by AAS, and the residual amounts of Pd were assumed to be on the support.

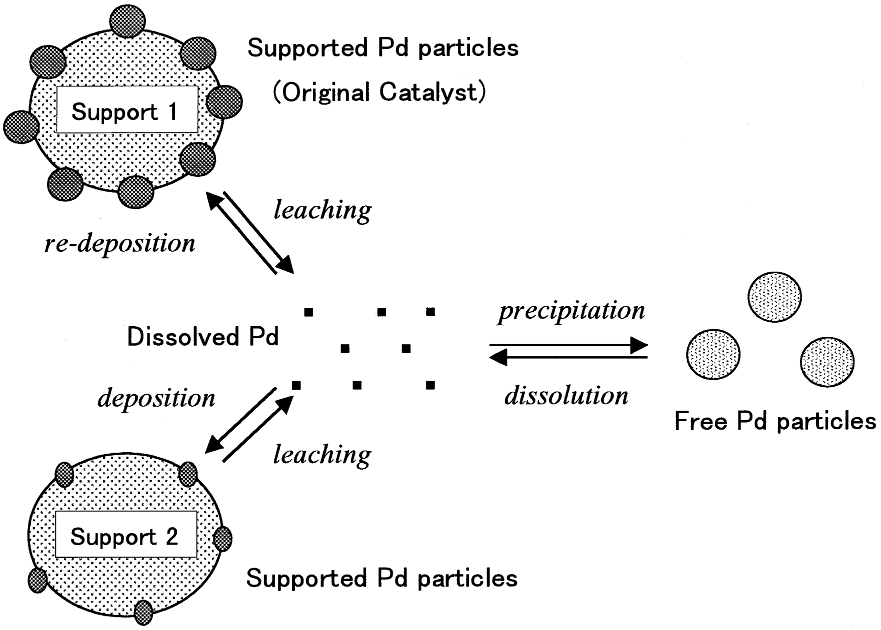

FIG. 2. Transfer of Pd species between support and solution during Heck reaction. Leaching from and deposition onto support and precipitation into free colloidal particles occur depending on reaction conditions and surface properties of support used.

that when C(1) was added, all Pd species transferred onto it and no free particles were formed at 100% conversion of iodobenzene. After the first run, the reaction mixture was centrifuged, and then the solid and liquid phases were separated by decantation. The residual solid mixture with a small quantity of the liquid phase, including the supported catalyst (Pd/C(1)) formed in situ and a small amount of sodium carbonate, was again mixed with fresh solvent, substrates, and bases. For the second and third runs, Pd dissolved in solvent and was working as catalyst, and it was recovered through the redeposition onto C(1) and recycled. In the absence of C(1), free colloidal Pd particles were formed and there were no Pd species remaining in solution after the completion of reaction. All Pd species were separated from the reaction mixture in the form of free colloidal Pd particles and were reusable. The same conversion was also achieved for the second run. The free colloidal Pd particles were dissolvable in new reaction solution, catalyzing the reaction smoothly. Carmichael *et al.* recently reported similar types of behavior for Pd particles in their three-phase Heck reaction (21). The effectiveness of colloidal Pd particles has been reported by a few authors (22, 23).

In conclusion, Pd exists in solution, on the support, and in the form of free colloidal particles during and after the Heck reaction. The transfer of Pd between these phases, as illustrated in Fig. 2, depends on the surface nature of the supports and reaction conditions used. The present results are significant for the development of recyclable Heck catalysts. It is reported elsewhere (12) that the concurrent use of inorganic and organic bases promotes the Pd deposition onto the support, and the substrate (iodobenzene) stabilizes the Pd species in NMP solvent although the details of the chemistry involved are not clear at present.

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