

Heck Reactions of Iodobenzene and Methyl Acrylate with Conventional Supported Palladium Catalysts in the Presence of Organic and/or Inorganic Bases without Ligands

Fengyu Zhao, Bhalchandra M. Bhanage, Masayuki Shirai, and Masahiko Arai*[a]

Abstract: The vinylation of iodobenzene with methyl acrylate has been studied with several supported palladium catalysts in *N*-methylpyrrolidone in the presence of triethylamine and/or sodium carbonate. The reaction can be performed in air without any solubilizing or activating ligands. It was found that significant amounts of palladium leach out into the solvent and these dissolved Pd species essentially catalyze the reaction. It is interesting, however,

that almost all the palladium species in the solution can redeposit onto the surface of the supports after the reaction has been completed (at 100 % conversion of iodobenzene). Thus, the catalysts were recyclable without loss of activity. The use of both inorganic and organic

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bases is very effective in the promotion of the palladium redeposition as well as in the enhancement of the reaction rate. For Heck reactions with bromobenzene and chlorobenzene it was found that the use of triethylamine and sodium carbonate increases the selectivity of the Heck coupling product (benzene is also produced for these two substrates), but the mixed bases do not affect the overall rate of reaction as much.

Introduction

The Heck reaction has received considerable attention in recent years as it offers a versatile method for the generation of new carbon–carbon bonds.^[1] The reaction is normally carried out with a palladium catalyst, a phosphine ligand, and a base in a homogeneous mode of operation. However, the reaction suffers from severe limitations that have so far precluded its wide-spread industrial application.^[2] Relatively large amounts of catalysts are needed for reasonable conversions and catalyst recycling is often hampered by the early precipitation of palladium black. A few approaches have been described to improve homogeneous catalyst systems by means of sterically hindered phosphine ligands,^[3a, 3b] a large excess of coordinating ligands,^[3a, 3c] and high-pressure conditions.^[3d, 3e]

In view of the practical and industrial applications, the use of heterogeneous catalysts may be promising. There are several reports on the use of free colloidal palladium particles^[4] and palladium catalysts dispersed on various supporting materials in the presence^[5] and absence^[6] of ligands. The latter catalysts may be concerned with an

important problem of the dissolution of palladium species into the solvent (leaching). Djakovich and Koehler have very recently given quantitative data for this palladium leaching from zeolite-supported palladium catalysts;^[6i] however, no other significant data has been reported. Augustine and O'Leary showed that in their Heck arylation, which used a carbon-supported palladium catalyst, the same reaction products were obtained as those with commonly used homogeneous catalysts.^[6f] Schmidt and Mametova used a silica-supported palladium catalyst for Heck reactions and indicated that the reaction proceeded in the liquid phase.^[6k] Mehnert et al. have recently prepared a new type of heterogeneous palladium catalyst on mesoporous MCM-41 material, and it has been shown to be active and recyclable for Heck reactions.^[6j] It is still felt, however, that a more complete investigation should be carried out on the usefulness of conventional supported metal catalysts for Heck reactions. The preparation of these catalysts is facile and some catalysts are commercially available; therefore, their use would be appreciated if they were effective Heck catalysts.

In the present work, we have used several ordinary supported palladium catalysts without any ligands for the Heck vinylation of iodobenzene with methyl acrylate in *N*-methylpyrrolidone (NMP). The reactions were conducted under various conditions to examine the factors that affect the rate of reaction as well as the extent of palladium leaching. It was found that the supported palladium leaches out into the

[a] Dr. M. Arai, F. Zhao, Dr. B. M. Bhanage, Dr. M. Shirai
Institute for Chemical Reaction Science
Tohoku University
Katahira, Aoba-ku, Sendai 980-8577 (Japan)
Fax: (+81) 22-217-5631
E-mail: marai@icrs.tohoku.ac.jp

solvent and that the reaction is mainly catalyzed with these dissolved palladium species. It is interesting to note, however, that the dissolved palladium species can redeposit onto the support after completion of the reaction so that the catalysts are recyclable without loss of activity. It is also interesting that the use of a mixed base of sodium carbonate and triethylamine not only increased the rate of reaction but also promoted the redeposition of the palladium species. To our knowledge, no work has yet been reported on the usefulness of such mixed bases for Heck reactions. Brief studies have also been made to compare the less reactive bromo- and chloro-substrates with iodobenzene.

Results and Discussion

The chief experiments were carried out with iodobenzene and the results on its vinylation with methyl acrylate are discussed in detail in the following. The results with bromo- and chloro-substrates are also reported briefly. The catalysts used in the present work are given in Table 1.

Reaction profiles and palladium leaching: The overall rate of the Heck vinylation of iodobenzene with methyl acrylate as well as the leaching of palladium have been found to depend on several factors. Under the conditions used, *trans*-methyl cinnamate was produced in 100% selectivity. Figure 1 shows time-conversion curves at 75 °C for 1% Pd/SiO₂ samples that were either reduced with H₂ at 450 °C for 3 h, calcined in air at 450 °C for 3 h, or were not treated before the reaction. The reduced sample was more active than the other two samples, which had similar activities. Figure 2 shows the conversion, the amount of Pd that leached out into the NMP solvent, and the amount of Pd remaining on the support during the reaction. For the samples examined, the rate of reaction increased as the amount of leached Pd increased. This indicates that the Heck reactions are mainly homogeneously catalyzed by Pd species dissolved in the solution, in accordance with the previous result of Schmidt and Mametova.^[6k] Marreto-Rosa et al. studied the carbonylation of allyl ethers with a charcoal-supported Pd catalyst.^[7] They believed that the reaction proceeded through homogeneous catalytic

Table 1. Supported Pd catalysts used in the present work.^[a]

Catalyst	Surface area of support [m ² g ⁻¹]	Reduction temperature [°C]	Degree of Pd dispersion
1 wt % Pd/SiO ₂	300	450	0.91 (1.0 nm) ^[b]
10 wt % Pd/C	893	200	0.18 (5.0 nm) ^[b]
1 wt % Pd/C	1181	200	0.54 (1.7 nm) ^[b]
1 wt % Pd/SM(Mg)	570	450	0.85 (1.1 nm) ^[b]

[a] The reduction was carried out for 3 h at the given temperatures. [b] Estimates of Pd particle sizes from an approximate expression of diameter (in nm) = 0.9/(degree of metal dispersion).^[13]

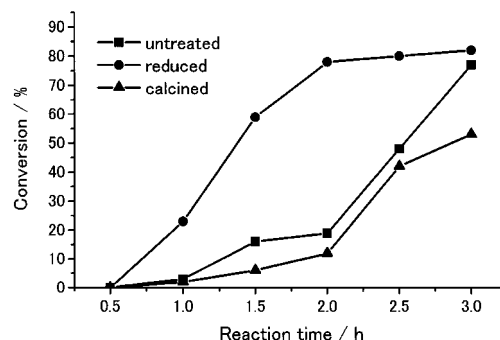


Figure 1. Time-conversion profiles of Heck reactions for reduced, calcined, or untreated 1% Pd/SiO₂ samples. Reaction conditions: 75 °C, catalyst 0.20 g (including 0.0188 mmol Pd), NMP 30 mL, iodobenzene and methyl acrylate 5 mmol each, triethylamine 5 mmol.

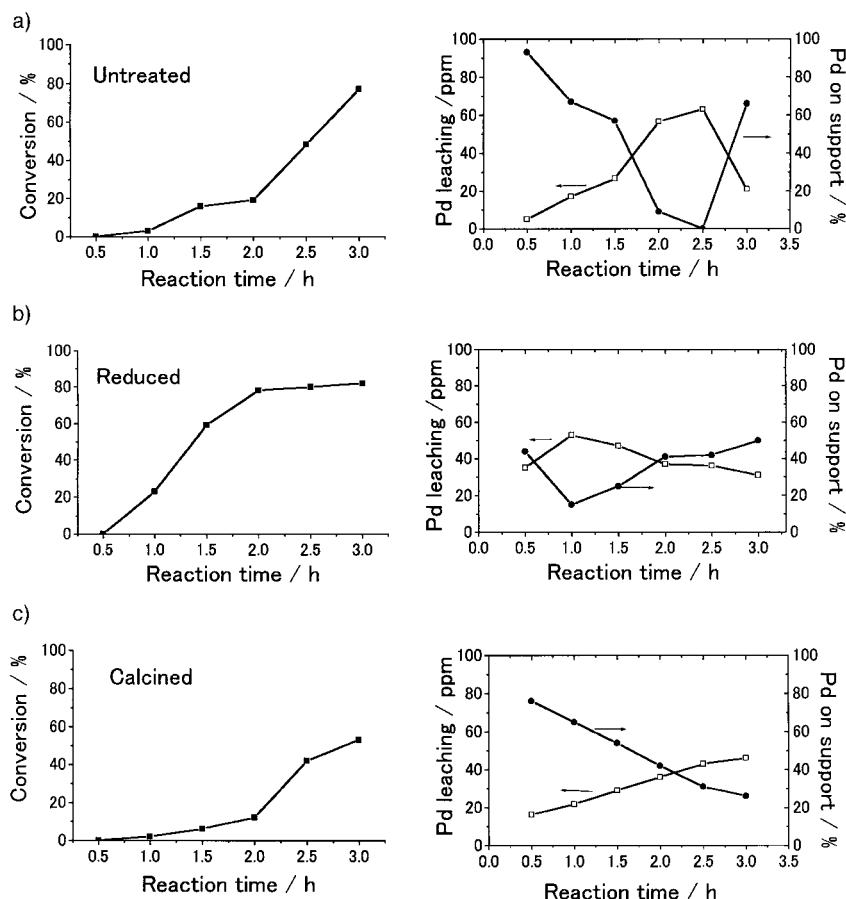


Figure 2. The conversion (left) and amount of Pd leached out into NMP or remaining on the support (right) as a function of time for a) untreated, b) reduced, and c) calcined 1% Pd/SiO₂ samples. The amounts of Pd on the support are relative values with respect to the initial amounts of Pd present in the catalysts. Reaction conditions: 75 °C, catalyst 0.20 g (including 0.0188 mmol Pd), NMP 30 mL, iodobenzene and methyl acrylate 5 mmol each, triethylamine 5 mmol.

Table 2. Effects of bases on the activity and Pd leaching of supported Pd catalysts.^[a]

Catalyst	Amount	Base	Time [h]	Conversion [%]	Pd leached into NMP [ppm]	Pd on support after reaction [%]
1 % Pd/SiO ₂	0.15 g (0.0141 mmol Pd)	TEA	1	100	23	0.49
1 % Pd/SiO ₂	0.15 g (0.0141 mmol Pd)	Na ₂ CO ₃	4	100	34	0.24
1 % Pd/SiO ₂	0.15 g (0.0141 mmol Pd)	TEA/Na ₂ CO ₃	0.5	100	4	0.91
10 % Pd/C	0.08 g (0.0752 mmol Pd)	TEA	0.5	100	9	9.6
10 % Pd/C	0.08 g (0.0752 mmol Pd)	Na ₂ CO ₃	0.5	47	60	7.5
10 % Pd/C	0.08 g (0.0752 mmol Pd)	Na ₂ CO ₃	4	100	10	9.6
10 % Pd/C	0.08 g (0.0752 mmol Pd)	TEA/Na ₂ CO ₃	0.5	100	4	9.8
1 % Pd/C	0.15 g (0.0141 mmol Pd)	TEA/Na ₂ CO ₃	0.5	100	4	0.91
1 % Pd/SM(Mg)	0.15 g (0.0141 mmol Pd)	TEA/Na ₂ CO ₃	0.5	100	6	0.87

[a] Pd/SiO₂ and Pd/SM(Mg) were reduced at 450 °C for 3 h and Pd/C at 200 °C for 3 h before the reaction; reaction conditions: 140 °C, NMP (30 mL), iodobenzene (5 mmol), methyl acrylate (5 mmol), triethylamine (TEA, 5 mmol), sodium carbonate (5 mmol). When both bases were used, the amounts of TEA and sodium carbonate were 5.0 mmol and 5.0 mmol, respectively.

Table 3. Effect of inorganic (sodium carbonate) and organic (triethylamine) bases on the Pd leaching of 10 % Pd/C catalyst.^[a]

Inorganic base [mmol]		Organic base [mmol]	Time [h]	Conversion [%]	Pd leached into NMP [ppm]	Pd on support after reaction [ppm]
initial	final					
5.0	2.5	0	4.0	100	10	9.6
5.0	2.5	5.0	0.5	100	4	9.8
2.5	0	1.0	0.5	100	4	9.8
2.5	0	2.5	0.5	100	4	9.8
2.5	0	5.0	0.5	100	4	9.8
1.25	0	2.3	1.0	80	60	7.5
1.25	0	3.0	0.5	100	6	9.8
0	0	1.0	0.5	100	4	9.8
0	0	7.5	0.5	100	8	9.7

[a] Reaction conditions: 140 °C, catalyst 0.08 g (including 0.0752 mmol Pd), NMP (30 mL), iodobenzene (5 mmol), and methyl acrylate (5 mmol).

pathways. For the allylation of aniline with allyl acetate with a Pd/C catalyst and triphenylphosphine, Bergbreiter and Chen also reported that the reaction was catalyzed by soluble palladium complexes.^[8] Furthermore, Figure 2 also shows that the reduced Pd species can leach out more easily to result in a higher rate of reaction, compared with oxidized Pd species on the calcined and untreated samples. It can be seen from Figure 2 that the amount of Pd dissolved in the solution decreased at higher conversion levels, which indicates the redeposition of Pd on the surface of SiO₂. Similar trends were also observed with the other catalysts.

Palladium leaching and redeposition: The amount of Pd which has leached into the solvent and that which has remained on support after the completion of Heck reactions are given in Table 2 for several catalysts at 140 °C. For 1 % Pd/SiO₂ and 10 % Pd/C catalysts, the use of a mixed base of triethylamine and sodium carbonate was very effective in reducing the amount of Pd remaining in the solution. The residual amount of Pd in the solution decreased from 23 or 34 ppm (for TEA and Na₂CO₃ alone, respectively) to 4 ppm (mixed base) and from 9 or 10 ppm (for TEA and Na₂CO₃ alone, respectively) to 4 ppm (mixed base) for the former and latter catalysts, respectively. That is, for 1 % Pd/SiO₂ and 10 % Pd/C catalysts, 91 % and 98 % of the initial metal loading can be recovered, respectively. For the other two catalysts, the levels of Pd leaching were also found to be very low when triethylamine and sodium carbonate were used together. The Pd leaching and redeposition may depend on the state of Pd dispersion (particle size and metal–support interactions) and/or the surface properties of support.

Therefore, it can be stated that Pd is leached from the support during the reaction and it can redeposit onto the surface of the support after completion of the reaction. Similar redeposition of Pd has recently been observed by Jayasree et al. for the synthesis of 2-arylpropionic acids by carbonylation with a supported Pd catalyst in the presence of phosphine ligands.^[9]

The influence of the ratio of organic:inorganic bases on Pd leaching was examined with 10 % Pd/C catalyst. Table 3 gives the levels of Pd leaching into the solvent and that remaining on the support after 100 % conversion of iodobenzene at 140 °C. When the two bases were used together, sodium carbonate was mainly consumed and triethylamine had no effect on the Pd leaching, which was 4 ppm. When the amount of sodium carbonate was 1.25 mmol, smaller than that of the substrates, the level of Pd leaching was somewhat larger, 6 ppm. Table 4 shows the influence of the amount of substrates at constant amount of the two bases at 140 °C. The amount of Pd dissolved in the solution was very high when unreacted iodobenzene remained. In contrast, it is lower by one order of magnitude when iodobenzene was completely consumed and it was independent of the amount of methyl acrylate.

Effects of temperature and supports on Pd redeposition:

Figure 3 shows the changes of the concentration of Pd dissolved in the solution and the amount of Pd on the support as a function of time at different temperatures for the 10 % Pd/C catalyst. Some time was needed to heat the reaction mixture, and the Heck reaction proceeded during the heating. The reaction was complete in 30 min after the reaction

Table 4. Effects of the substrate concentrations on the Pd leaching of 10% Pd/C catalyst.^[a]

Iodobenzene [mmol]		Methyl acrylate [mmol]		Iodobenzene conversion [%]	Pd leached into NMP [ppm]	Pd on support after reaction [%]
initial	final	initial	final			
5.0	3.5	1.2	0	34	50	8.0
5.0	3.0	2.0	0	40	30	8.8
5.0	0	6.0	1.0	100	4	9.8
5.0	0	10.0	5.0	100	5	9.8
10.0	0	10.0	0	100	5	9.8
20.0	0	21.0	1.0	100	4	9.8

[a] Reaction conditions: 140°C, catalyst 0.08 g (including 0.0752 mmol Pd), NMP (30 mL), triethylamine (1 mmol), sodium carbonate (2.5 mmol), reaction time 30 min.

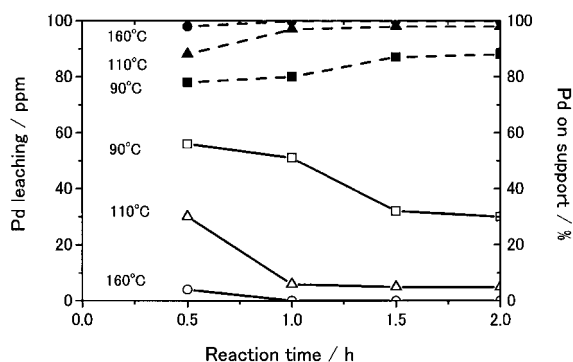


Figure 3. The changes in the concentration of Pd species in NMP (open symbols) and the amount of Pd present on support (solid symbols) as a function of time at different temperatures for the 10% Pd/C catalyst. The amounts of Pd on the support are relative values with respect to the initial amount of Pd present in the catalyst. Reaction conditions: catalyst 0.08 g (including 0.0752 mmol Pd), NMP 30 mL, iodobenzene and methyl acrylate 5 mmol each, triethylamine 1 mmol, sodium carbonate 2.5 mmol.

mixture reached the desired temperatures of 90, 110, and 160°C. The time given in Figure 3 is that which had elapsed after the desired temperatures were attained. The residual amount of Pd in the solution at 30 min was small and it decreased more rapidly to a very low level when the temperature was higher, that is, the redeposition of Pd on the support is faster at higher temperatures.

In Figure 4, three supports are compared with respect to the redeposition of Pd at 160°C. The redeposition depends on the nature of supports used, and it proceeds more rapidly on the carbon support than the others. Previously, Augustine and O'Leary used several supporting materials for Pd and they indicated the effect of their acid/base properties on the regioselectivity for the Heck arylation of *n*-butyl vinyl ether and benzoyl chlorides.^[6g] Djakovich and Koehler reported the influence of the type of zeolite on the leaching of Pd.^[6i]

Catalyst recycling: The same 10% Pd/C catalyst was used for several reactions, each of which was conducted up to 100% conversion under the following conditions: catalyst 0.08 g, iodobenzene and methyl acrylate 5 mmol each, triethylamine 1 mmol, sodium carbonate 2.5 mmol, NMP 30 mL, temperature 160°C, time 30 min. After each run, the reaction mixture was centrifuged and the liquid mixture was decanted. The residual catalyst was again mixed with fresh solvent, substrates, and bases. The catalyst could be reused for four runs while retaining the same activity and selectivity as well as without loss of the active Pd species. These results are

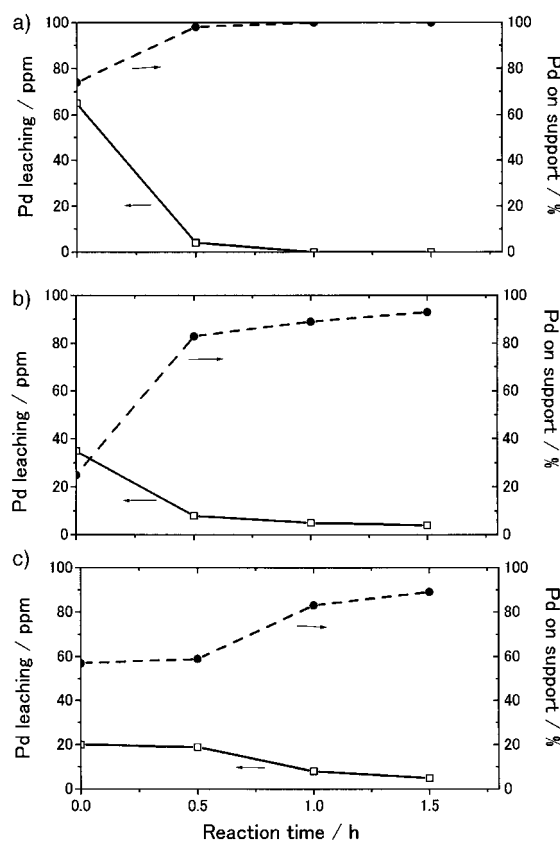


Figure 4. The changes in the concentration of Pd species in NMP (solid line) and the amount of Pd present on the support (dashed line) as a function of time at 160°C for Pd catalysts on different supports: a) 10% Pd/C; b) 1% Pd/SiO₂; c) 1% Pd/SM(Mg). The amounts of Pd on the support are relative values with respect to the initial amounts of Pd present in the catalysts. Reaction conditions: 10% Pd/C catalyst 0.08 g (including 0.0752 mmol Pd), 1% Pd/SiO₂ and 1% Pd/SM(Mg) 0.15 g (including 0.0141 mmol Pd), NMP 30 mL, iodobenzene and methyl acrylate 5 mmol each, triethylamine 1 mmol, sodium carbonate 2.5 mmol.

important from a practical point of view. The ordinary supported Pd catalysts are thermally stable at 160°C or above, at which temperature active organometallic Pd complexes cannot be used.

Nature of the reaction processes: The present Heck reaction system is homogeneous even though the heterogeneous catalysts are used, in accordance with the previous result of Schmidt and Mametova.^[6k] The results observed may be explained in part by a homogeneous Heck reaction mechanism.^[1] The reaction is catalyzed mainly with the Pd species in

the liquid phase. It is easier for the Pd from the H₂-reduced catalyst to leach into the solvent compared with the unreduced and calcined catalysts (Figures 1 and 2). In addition, active Pd⁰ species may be more easily formed in the solution with the first catalyst than with the last two. The NMP solvent and triethylamine could be involved in the formation of such active species. For homogeneous Heck reactions in NMP, the rate of reaction is higher in the absence of a triphenylphosphine ligand than in the presence of this ligand. This suggests the formation of active Pd⁰ complexes with the NMP molecules.^[10] Triethylamine is a reducing agent for the formation of active Pd⁰ species, and thus increases the rate of reaction. The aryl halide can react with Pd to form a [Pd–PhI] complex; this would also promote Pd leaching.

After the completion of the reaction, the Pd species can redeposit onto the supports and the catalysts are recyclable. The residual amount of Pd species in the solvent is much less when triethylamine and sodium carbonate are used at the same time. The latter is mainly involved in the Heck reaction while the former enhances the rate of reaction (Table 2). The Pd redeposition is influenced by triethylamine in the solution while it is not influenced by sodium carbonate. Interactions may exist between triethylamine and dissolved Pd species to produce some complexes which prevent the redeposition of Pd onto the support. In addition, there is a possibility that the base adduct (HET₃NI) formed is adsorbed by the supports^[6] and then hinders the Pd redeposition. The amount of Pd species in the solution is large when iodobenzene is present. The formation of a [Pd–PhI] complex would also hinder the redeposition of the Pd species.

Application to bromo and chloro substrates: For practical purposes, it is important to use the less reactive but cheaper bromo- and chloro-substrates, rather than iodo-substrates. Efforts are still being made towards the activation of these substrates in homogeneous^[11] and heterogeneous^[6] catalytic reactions. The supported Pd catalysts are stable at high temperatures, which may be necessary for Heck reactions of these less reactive substrates. Therefore, we briefly examined the effect of the organic and inorganic mixed bases on the Heck vinylation reaction of bromobenzene and chlorobenzene with methyl acrylate at 160 °C (Table 5). For either bromobenzene or chlorobenzene, the overall rate of reaction is promoted by the use of the mixed bases, similar to the case of iodobenzene; however, this effect is not so remarkable.

Unfortunately, for these substrates, the dominating reaction was dehalogenation so that the main product was benzene. Although the selectivity of the Heck coupling product is low, the presence of sodium carbonate did increase the yield. The amounts of Pd which leached into the solvent were larger for the mixed bases and sodium carbonate than those for triethylamine, for which the Pd in the solution is very low so that there was very little Heck coupling. Thus, it can be assumed that the Heck coupling is homogeneously catalyzed by the dissolved Pd species, while the dehalogenation reaction occurs on the surface of the Pd particles. The results given in Table 5 indicate that the overall rate of reaction is not low, but further efforts are needed to improve the Heck selectivity. The effects of different combinations of other inorganic bases (such as potassium carbonate and caesium carbonate) and triethylamine have been investigated in our laboratory. The basic reaction mechanism would be the same for the three substrates, but the relative rates of the elementary steps involved may depend on the kinds of substrate and base used. This may result in the differences in the effects of the mixed bases for iodo-, bromo-, and chloro-substrates. In their recent work on a heterogeneous Pd catalyst, Mehnert et al. have reported that the Heck coupling selectivity is 82 % at 39 % conversion for bromobenzene with styrene and 40 % at 16 % conversion for chlorobenzene with *n*-butyl acrylate at 170 °C.^[6]

Conclusions

The following conclusions are drawn from the present results on the Heck reactions of iodobenzene and methyl acrylate in NMP with organic and inorganic bases with supported Pd catalysts without any ligands in air (points 1–7) as well as for the Heck reactions with bromobenzene and chlorobenzene (points 8 and 9).

- 1) The reaction is homogeneous and catalyzed by Pd species dissolved in NMP under the reaction conditions used.
- 2) The reduced Pd species are more easily leached out into the solvent compared with the oxidized species. This results in a higher rate of reaction.
- 3) The Pd species in solution can redeposit onto the supports only after the reaction is complete.
- 4) The Pd redeposition is promoted by the use of a mixed base of triethylamine and sodium carbonate.

Table 5. Results of Heck reactions of bromobenzene/chlorobenzene and methyl acrylate with 10 % Pd/C catalyst.^[a]

Substrate	Base	Time [h]	Conversion [%]	Selectivity ^[b] [%]	Pd leached into NMP [ppm]	Pd on support after reaction [%]
bromobenzene	TEA	12	75	7	1	9.9
	TEA/Na ₂ CO ₃	12	96	14	40	8.4
	Na ₂ CO ₃	12	88	22	40	8.4
chlorobenzene	TEA	18	55	0	2	9.9
	TEA/Na ₂ CO ₃	18	69	3	42	8.3
	Na ₂ CO ₃	18	59	4	42	8.3

[a] The catalyst was reduced at 200 °C for 3 h before reaction. Reaction conditions: 160 °C, catalyst: 0.08 g (including 0.0752 mmol Pd), NMP (30 mL), bromobenzene/chlorobenzene (5 mmol), methyl acrylate (5 mmol), triethylamine (TEA, 5 mmol), sodium carbonate (5 mmol). When both the bases were used, the amounts of TEA and sodium carbonate were 1.0 mmol and 2.5 mmol, respectively. [b] Selectivity = methyl cinnamate/(methyl cinnamate + benzene).

- 5) The Pd redeposition depends on temperature and support used.
- 6) The catalysts, in particular 10 wt % Pd/C, can be effectively recycled without loss of Pd species.
- 7) The supported catalysts are thermally stable and therefore reactions can be conducted at the relatively high temperature of 160 °C.
- 8) The use of the mixed bases does not change the overall rate of reaction very much.
- 9) The presence of sodium carbonate increases the selectivity of the Heck coupling product (for these two substrates, dehalogenation predominantly occurs to produce more benzene than methyl cinnamate).

Experimental Section

Catalyst: A commercial sample of 10% Pd on activated carbon was purchased from Wako Pure Chemicals Industries. Other 1% Pd catalysts were prepared by ion exchange, with $[\text{Pd}(\text{NH}_3)_4\text{Cl}_2]$ as the precursor, with SiO_2 (Aldrich Chemical Company, DAVISIL grade 646, 35–60 mesh), activated carbon (Nippon Chromato Works, 80–100 mesh), and a magnesium-containing smectite-like porous material (denoted by SM(Mg)) prepared by a hydrothermal method in our laboratory.^[12a,b] The Pd/C samples were reduced under a flow of hydrogen at 200 °C for 3 h or at 450 °C for 3 h; these reduced samples were stored in a desiccator. The details of preparation procedures for these catalysts is described elsewhere.^[12a,c] The surface areas of the supports were determined by the BET nitrogen adsorption method. The areas of exposed palladium atoms were measured by hydrogen adsorption at room temperature (Table 1).

Heck reactions: The Heck reactions were carried out in a 100 ml autoclave under an ambient atmosphere. Commercial (Wako Pure Chem. Ind.) iodobenzene (or bromobenzene, chlorobenzene), methyl acrylate, NMP solvent, triethylamine, and sodium carbonate were used. The reaction was monitored at various time intervals by analyzing the reaction mixture with a gas chromatograph (GC, Yanaco G3800, Silicon OV-1, 6 m) equipped with a flame ionization detector. Iodobenzene, methyl acrylate, and triethylamine were mixed with NMP solvent (30 mL) and a small quantity of this mixture was first analyzed by GC. The liquid mixture was placed in the autoclave and then the catalyst and sodium carbonate (if necessary) were added. The reaction mixture was heated to the desired reaction temperature, while vigorously agitating with a magnetic stirrer. During the reaction, small quantities of the reaction mixture were sampled and analyzed by GC. The conversion was determined from the amount of iodobenzene consumed and error limits for the %-conversion data were $\pm 3.0\%$ on account of the reproducibility of the data for repeated runs. After the reaction was complete, the mixture was left to stand for ≈ 15 min. The solid materials precipitated and the liquid phase, which included NMP, triethylamine, substrates, products, and HI-base adducts, was separated by decantation. The residual solid mixture (including catalyst and sodium carbonate) and a small quantity of liquid were washed with acetone a few times and then dried in air. The catalyst and inorganic base were separated by size, the former being fine powder, and the weight of the residual sodium carbonate was measured. Within experimental error, the weight of the catalyst did not change after the reaction. The amount of Pd leaching out into the solution was measured by atomic absorption spectroscopy. Under the conditions used, the concentrations of Pd determined included errors of less than ± 0.5 ppm.

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