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# The leaching and re-deposition of metal species from and onto conventional supported palladium catalysts in the Heck reaction of iodobenzene and methyl acrylate in *N*-methylpyrrolidone

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## Abstract

When supported palladium catalysts are used for Heck vinylation of iodobenzene with methyl acrylate in *N*-methylpyrrolidone (NMP) in the presence of triethylamine and sodium carbonate bases, the reaction proceeds homogeneously with dissolved active palladium species that are formed through coordination of NMP and triethylamine with palladium. These active species easily react with iodobenzene (oxidative addition), beginning the catalytic cycle of Heck coupling. The last step of catalyst regeneration takes place with the action of sodium carbonate. The active palladium species are not stable and deposit the metal to support when they cannot find iodobenzene to react in the reaction mixture after this substrate is completely consumed. The re-deposition of palladium occurs on the surfaces of bare support and/or palladium particles remaining on it, depending on the nature of support surface and the number and size of residual metal particles. The growth of palladium particles has been observed after the reuse of catalyst in some case. However, the supported catalysts are recyclable without loss of activity.

*Keywords:* Heck vinylation; Heterogeneous catalysis; Palladium; Leaching; Re-deposition

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## 1. Introduction

Heck reaction has received considerable attentions in recent years as it offers versatile method for generating new carbon–carbon bond [1–5]. The reaction is normally carried out with a palladium catalyst, a phosphine ligand and a base in homogeneous mode of operation. However, the reaction suffers from some limitations that have so far precluded widely spread industrial applications. A relatively large amount of catalyst is needed for reasonable conversion and catalyst recycling is often hampered by early precipitation of palladium black [1,6]. Recently, highly efficient homogeneous catalysts have been reported by Brunel et al. [7].

In view of practical applications, the use of heterogeneous catalysts is important for the catalyst separation and recycling. However, only sporadic works have been reported on heterogeneous Heck reactions, and conventional supported catalysts are often concerned with a problem of leaching of catalytic active species like costly palladium metal. Djakovitch et al. examined Heck reactions catalyzed with zeolite-supported palladium catalysts and reported some quantitative data of palladium leaching [8]. Kiviaho et al. [9] reported that

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the catalysts of palladium supported on modified silica supports, such as $Pd[P(C_6H_5)_3]_2/SiO_2$–Ti–$(NH)_2$ and $Pd[P(C_6H_5)_3]_2/SiO_2$–Sn–$(NH)_2$, could catalyze the Heck vinylation of iodobenzene with methyl acrylate; these catalysts were stable with very less amounts of Pd leaching and were reused for several times. Barreto-Rosa et al. [10] studied carbonylation of allyl ethers using a charcoal-supported palladium catalyst and proposed that the reaction proceeded through homogeneous catalytic pathways. Bergbreiter and Chen [11] reported that the allylation of aniline with allyl acetate with a Pd/C catalyst in the presence of triphenylphosphine (TPP) was also catalyzed by soluble palladium complexes.

The leaching of active species is a serious problem for supported metal catalysts, which prohibits the catalyst separation and recycling. Although the literature contains several references to the leaching of supported palladium catalyst, the investigation has not been extended beyond comparing the leaching levels for several catalysts and the mechanism of palladium leaching has not been discussed in detail. From the view of application, it is significant to study the mechanism of catalyst leaching in order to control the leaching process and level. So the palladium leaching has further been studied in the present work. We have found that when the vinylation reactions of iodobenzene with methyl acrylate are catalyzed with $Pd/SiO_2$ and Pd/C catalysts, the rate of reaction depends on the amount of palladium dissolved in the solution; namely, the reactions proceed homogeneously with these dissolved palladium species [12]. The same results were also reported in a previous communication of Shmidt and Mametova [13]. It is worth to note that the dissolved palladium species can re-deposit on supports after the completion of reaction in our reaction system and the catalysts are recyclable without loss in activity [12]. The mechanism of palladium leaching and re-deposition will be discussed in the present work.

## 2. Experimental

### 2.1. Catalyst

A commercial 10 wt.% Pd on activated carbon sample was purchased from Wako Pure Chem. Ind. A 1.8 wt.% $Pd/SiO_2$ catalyst was prepared by ion exchange with $Pd(NH_3)_4Cl_2$ as precursor using $SiO_2$ (Aldrich, Davisil grade 646, 35–60 mesh). The Pd/C sample was reduced by flowing hydrogen at 200 °C for 3 h. After ion exchange, $Pd/SiO_2$ sample was dried under dynamic evacuation (as-prepared catalyst). Then it was reduced by hydrogen or calcined in air at 450 °C for 3 h (reduced and calcined catalysts, respectively). These samples were stored in a desiccator before reaction. The details of preparation procedures for those catalysts are described elsewhere [14,15].

### 2.2. Heck reaction

#### 2.2.1. Materials

Catalyst of $Pd(OAc)_2$, ligand of TPP, reactants of iodobenzene and methyl acrylate, solvents of *N*-methylpyrrolidone (NMP) and toluene, bases of triethylamine and sodium carbonate were purchased from Wako Pure Chem. Ind. and were used without further purification.

#### 2.2.2. General reaction procedures

The Heck reactions were carried out in a 100 ml autoclave under ambient atmosphere. Iodobenzene, methyl acrylate and a certain amount of triethylamine were mixed with solvent of NMP or toluene. Before reaction, a small quantity of this mixture was sampled and analyzed by gas chromatograph (GC). The liquid mixture was put into the autoclave and then 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. The reaction was monitored at various time intervals by analyzing the reaction mixture using GC (Yanaco G3800, Silicon OV-1, 6 m) with flame ionization detector. The conversion was determined from the amount of iodobenzene consumed and error limits for the percent-conversion data were ±3.0% due to the reproducibility of the data for repeated runs. The amount of Pd leaching out into the solution was measured using atomic absorption spectroscopy. Under the conditions used, the concentrations of Pd determined included errors less than ±0.5 ppm.

#### 2.2.3. Homogeneous reactions

Typical reaction conditions: iodobenzene, methyl acrylate, 5 mmol each; triethylamine, 0.1∼5 mmol;

catalyst $Pd(OAc)_2$, 0.05 mmol; ligand TPP or NMP, 0.1 mmol; solvent toluene or NMP, 30 ml; reaction temperature, 80–100 °C; reaction time 2 h.

### 2.2.4. *Heterogeneous reactions*

The $Pd/SiO_2$ catalyst was subjected to a few pretreatments before reaction. A 150 mg of $Pd/SiO_2$ sample (as-prepared, reduced and calcined, including 0.0254 mmol Pd) was immersed in NMP (30 ml) solvent or the mixture of NMP (30 ml) and $Et_3N$ (5 mmol) at room temperature for 2 h, then small quantities of the mixture were sampled and analyzed by atomic absorption spectroscopy to determine the Pd leaching level on these pretreatments. Then, the reactants of iodobenzene (5 mmol), methyl acrylate (5 mmol) and base $Et_3N$ (5 mmol, if necessary) were added to the mixture, and the mixture was put into the reactor. The reaction was started by heating the mixture to the desired temperature. For catalyst recycling test, the first run was carried under the reaction conditions: iodobenzene, methyl acrylate, 5 mmol each; triethylamine, 1 mmol; catalyst 10 wt.% Pd/C catalyst, 80 mg (0.0752 mmol Pd); sodium carbonate, 2.5 mmol; solvent NMP, 30 ml at 160 °C. After the first run was completed, the reaction mixture was cooled to room temperature, and the reaction mixture was made to stand for about 15 min until the solid materials precipitated, then the liquid phase was separated by decantation, which included NMP, triethylamine, substrates, products and HI-base adducts. The residual solid mixture with a small quantity of liquids, including catalyst and sodium carbonate, was reused directly for the subsequence reactions. After fresh reactants were added, the subsequent reaction was conducted under the same reaction conditions. The size of supported palladium particles before and after recycling was measured by using JEM-2000EX electron microscope operated in the bright field mode and X-ray diffraction (XRD) with Shimadzu XD-D1.

## 3. Results and discussion

For the Heck reactions of iodobenzene and methyl acrylate with conventional supported palladium catalysts, the palladium leaching and re-deposition were shown to occur, as reported previously [12]. In the following sections, governing factors and mechanisms of these palladium mass transfer phenomena will be discussed from the results with both heterogeneous and homogeneous palladium catalysts.

### 3.1. *Palladium leaching*

It was reported that the rate of homogeneous Heck reaction with $Pd(OAc)_2$ catalyst without any ligands in NMP solvent was larger than that with $Pd(OAc)_2$ catalyst and TPP ligand [16]. For these experiments, $Et_3N$ was used as a base. In heterogeneous Heck reactions with supported palladium catalysts, NMP and $Et_3N$ were also used as a solvent and a base, respectively. To examine the influence of NMP and

Table 1

Influence of pretreatments of 1.8 wt.% $Pd/SiO_2$ catalyst on conversion and palladium leaching for Heck vinylation of iodobenzene with methyl acrylate in NMP

| Catalyst | Pretreatment[a] | Conversion[b] (%) | Palladium leaching level (ppm) | |
|---|---|---|---|---|
| | | | Before reaction | After reaction |
| Reduced | NMP + $Et_3N$ | 87 | 40 | 22 |
| | NMP | 64 | 19 | 58 |
| As-prepared | NMP + $Et_3N$ | 56 | 18 | 65 |
| | NMP | 40 | 8 | 67 |
| Calcined | NMP + $Et_3N$ | 46 | 26 | 46 |
| | NMP | 35 | 12 | 38 |

[a] For pretreatment procedures, see Section 2.

[b] Reaction conditions: iodobenzene, methyl acrylate, triethylamine, 5 mmol each; NMP, 30 ml; catalyst, 150 mg (Pd 0.0254 mmol); temperature, 80 °C; reaction time, 2 h.

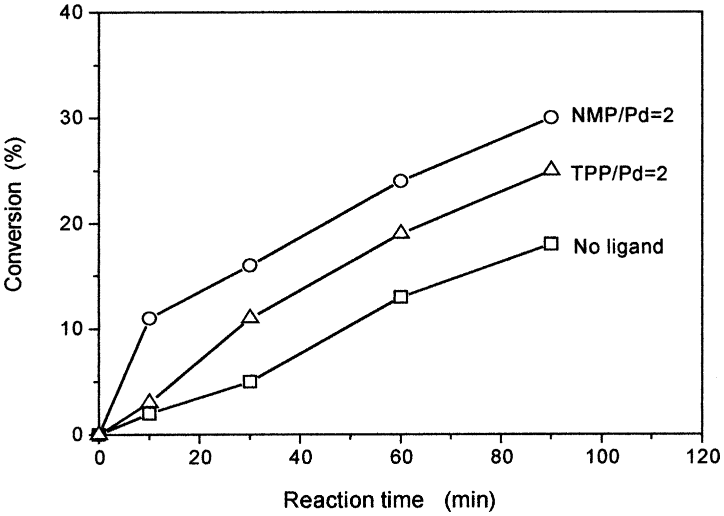
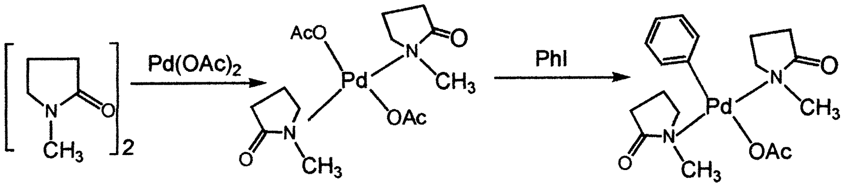


Fig. 1. Homogeneous Heck vinylation of iodobenzene with methyl acrylate in toluene using $Pd(OAc)_2$ catalyst in the presence and absence of NMP or TPP ligand. Reaction conditions: iodobenzene, methyl acrylate, triethylamine, 20 mmol each; total volume of reaction mixture, 15 ml; catalyst $Pd(OAc)_2$, 0.05 mmol; temperature, 95 °C.

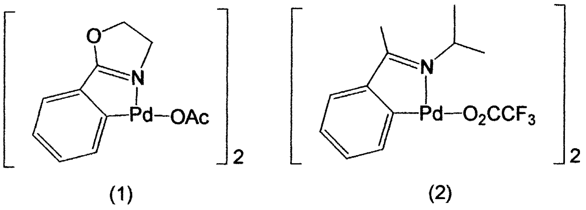
$Et_3N$ on the palladium leaching, a 1.8 wt.% $Pd/SiO_2$ catalyst has been pretreated with NMP and/or $Et_3N$ before reaction. The results of these pretreatments on conversion and leaching level obtained are shown in Table 1. The leaching of palladium into NMP is enhanced by the presence of $Et_3N$ and the leaching level is higher for hydrogen-reduced catalyst than those for calcined and as-prepared catalysts, in which supported palladium species are in some oxidation state. These results indicate that the palladium leaching occurs through interactions of NMP and $Et_3N$ with the metal and this process is easier to take place for reduced palladium than for oxidized palladium.

To further examine the influence of NMP, homogeneous Heck vinylation of iodobenzene with methyl acrylate has been carried out in toluene solvent in the presence of a ligand quantity of TPP or NMP ($TPP/\mathrm{Pd} = \mathrm{NMP}/\mathrm{Pd} = 2$). The time–conversion curves obtained are shown in Fig. 1, indicating that the addition of NMP increases the rate of reaction more markedly compared with TPP ligand. It can then be assumed that the NMP molecules produce a more active complex with palladium than do TPP ligands. A possible form of such a complex is proposed in Scheme 1, which is produced through interaction between N of NMP and Pd. Ohff et al. [17] have recently developed a new phosphine-free, nitrogen-based ligand for Heck reactions, from which new dimeric imine palladium complexes are formed as shown in Scheme 2. Their work supports the possibility of the formation of the complex given in Scheme 1.

It was shown that the presence of mixed bases of $Et_3N$ and $Na_2CO_3$ enhanced the rates of Heck reaction, $Na_2CO_3$ was mainly consumed, and the



Scheme 1. A possible complex formed from NMP molecule and $Pd(OAc)_2$ catalyst during Heck vinylation of iodobenzene in NMP.



Scheme 2. Phosphine-free, nitrogen-based ligands for Heck reactions [17].

amounts of $Et_3N$ from 1∼5 mmol had no effect on the reaction [12]. $Na_2CO_3$ was unable to play a role in the leaching of palladium and in the formation of active palladium complexes, which were produced with NMP molecules only when $Et_3N$ was not used. In the absence of $Na_2CO_3$, $Et_3N$ took part in the formation of soluble active palladium complexes at the first step of reaction and in the regeneration of these species at the last step of catalytic cycle. When the organic and inorganic bases were used at the same time, they should have separately played their own roles, $Et_3N$ producing the active palladium complexes and $Na_2CO_3$ regenerating them. This may be responsible for the larger rate of reaction in the presence of these two bases than the rate with a single base of $Na_2CO_3$. Another responsible factor may be a difference in the reactivity between the palladium complexes formed from both NMP and $Et_3N$ and from NMP alone.

To further discuss the role of $Et_3N$, we have examined the influence of the addition of small amount of $Et_3N$ to homogeneous Heck reaction in the presence of $Na_2CO_3$. The results of time–conversion curves obtained are shown in Fig. 2. The rate of reaction increases with an increase in the amount of $Et_3N$ added but it does not change so much when the $Et_3N$/Pd ratio increases from 10 to 12. These ratios of 10 and 12 seem to be large for a coordination number with a palladium. In addition to the role of ligand, another role of $Et_3N$ should be taken into consideration, which is a reducing agent to reduce the catalyst from palladium(II) to palladium(0) active species. Beller and Riermeier [18] also reported the influence of the coordination of organic base amine with palladium on the rate of reaction and product distribution in Heck reactions. Herrmann et al. [19] reported that the coordination of amine with palladium blocked the free coordination sites of palladium, which improved the regio-selectivity towards internal olefins.

It is assumed from the mentioned results that the palladium leaching is caused by the coordination of solvent NMP and organic base $Et_3N$ with palladium

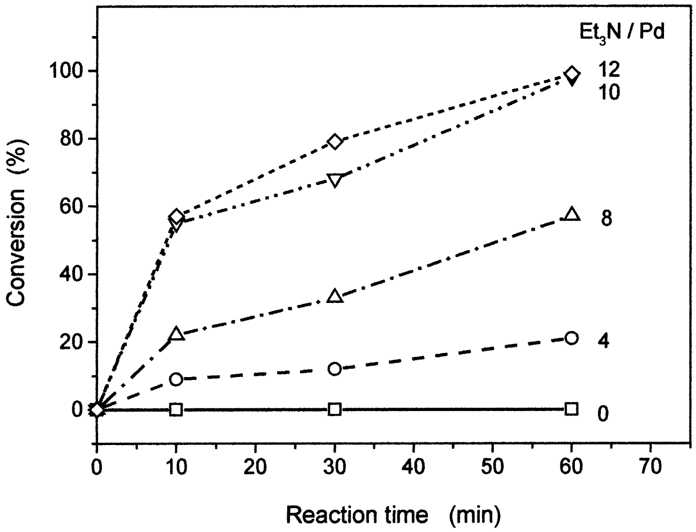


Fig. 2. Influence of addition of small quantity of triethylamine on homogeneous Heck vinylation of iodobenzene with methyl methacrylate in NMP in the presence of $Na_2CO_3$ base using $Pd(OAc)_2$ catalyst. Reaction conditions: iodobenzene, methyl acrylate, 5 mmol each; NMP, 30 ml; $Na_2CO_3$, 2.5 mmol; catalyst $Pd(OAc)_2$, 0.05 mmol; temperature, 100 °C.

to form palladium complexes soluble in the reaction solution. These palladium complexes are active species and the present Heck vinylation mainly proceeds homogeneously in the solution although the catalyst is originally heterogeneous. In addition, the formation of such a complex is easier to occur with reduced catalyst than oxidized catalysts, for which the complex formation and leaching should follow the reduction of oxidized palladium species by some agents like $Et_3N$. It is reasonable to assume that the oxidized palladium species are more resistant to the leaching from supports by NMP and $Et_3N$ than the reduced ones.

### 3.2. Palladium re-deposition

After the reaction completes (iodobenzene completely disappears), palladium goes back to the surface of support. Since all the palladium species do not leach out into solvent, the dissolved palladium could re-deposit on two possible sites, which are bare surface of support and surface of palladium particles remaining on support. The size of palladium particles has been examined before and after reaction by XRD and TEM for a 10 wt.% Pd/C catalyst. In this experiment, a higher reaction temperature of 160 °C was used because the re-deposition occurred more rapidly. Fig. 3 shows XRD patterns, indicating that the palladium(1 1 1) and (2 0 0) diffraction peaks became sharper and so the palladium particles grew after reaction. The particle growth was also supported by TEM results given in Fig. 4. For this catalyst, therefore, the re-deposition occurs preferentially on the surface of residual palladium particles than the bare surface of support. Probably this would be different depending on such factors as the nature of support surface and/or the number and size of residual metal particles. It was previously indicated that the surface functional groups on carbon and silica were significant for the palladium re-deposition, which were carboxyl and hydroxyl groups, for example [20].

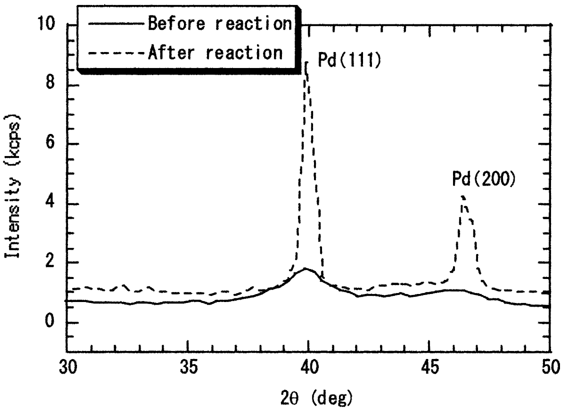


Fig. 3. XRD of 10 wt.% Pd/C catalyst before and after Heck vinylation of iodobenzene with methyl acrylate in NMP at 160 °C.

### 3.3. Mechanism of Heck reaction with supported palladium catalyst

From the results described earlier, the mechanism of the Heck vinylation of iodobenzene with supported palladium catalyst in NMP solvent with $Et_3N$ and $Na_2CO_3$ bases is proposed, which is shown in Scheme 3. At the first step, soluble palladium complexes are formed by the coordination with polar solvent NMP and/or organic base $Et_3N$, and these are catalytically active species. When iodobenzene exists, its oxidative addition to these palladium complexes occurs and the reaction continues to go homogeneously in the solvent according to the accepted mechanism of Heck reaction [4]. When iodobenzene is completely consumed and absent in the reaction mixture, however, the complexes are not so stable that the palladium will go back to the surface of support (re-deposition). At the last step of reductive elimination, $Na_2CO_3$ mainly acts rather than $Et_3N$. This should not affect the total rate of reaction since the rate with the mixed bases is not so different from that with $Et_3N$ alone. We have observed a higher rate of reaction in the presence of both $Et_3N$ and $Na_2CO_3$ compared with that using $Na_2CO_3$ only. This may be due to the differences in the leaching level and/or in the reactivity between the palladium complexes formed with NMP and $Et_3N$ and those with NMP.

For 10 wt.% Pd/C catalyst used in the present work, the palladium re-deposition occurs preferentially on the surface of residual palladium particles and so the size of metal particles increases after reaction.

The palladium leaching occurs more easily for hydrogen-reduced sample compared with as-prepared and calcined samples. For the latter two samples, oxidized palladium species should be the first reduced to palladium(0) species and then form the complexes

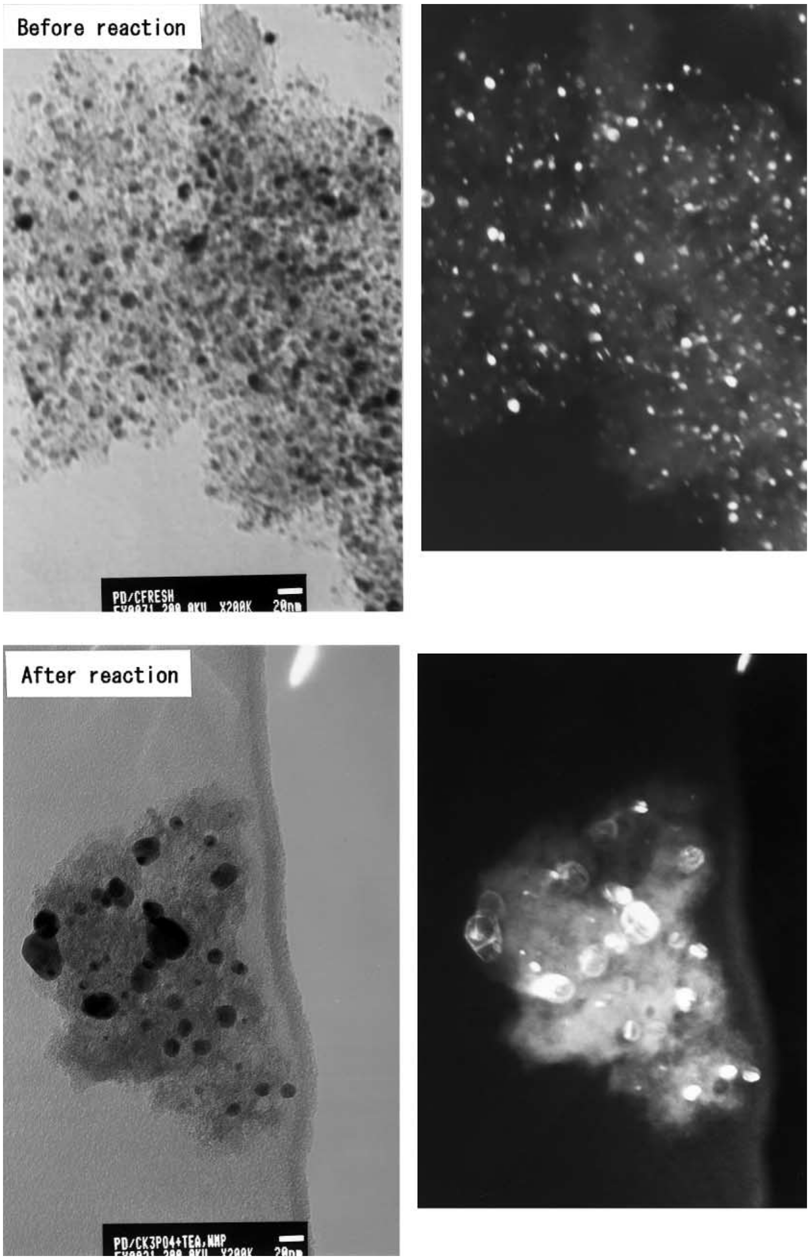
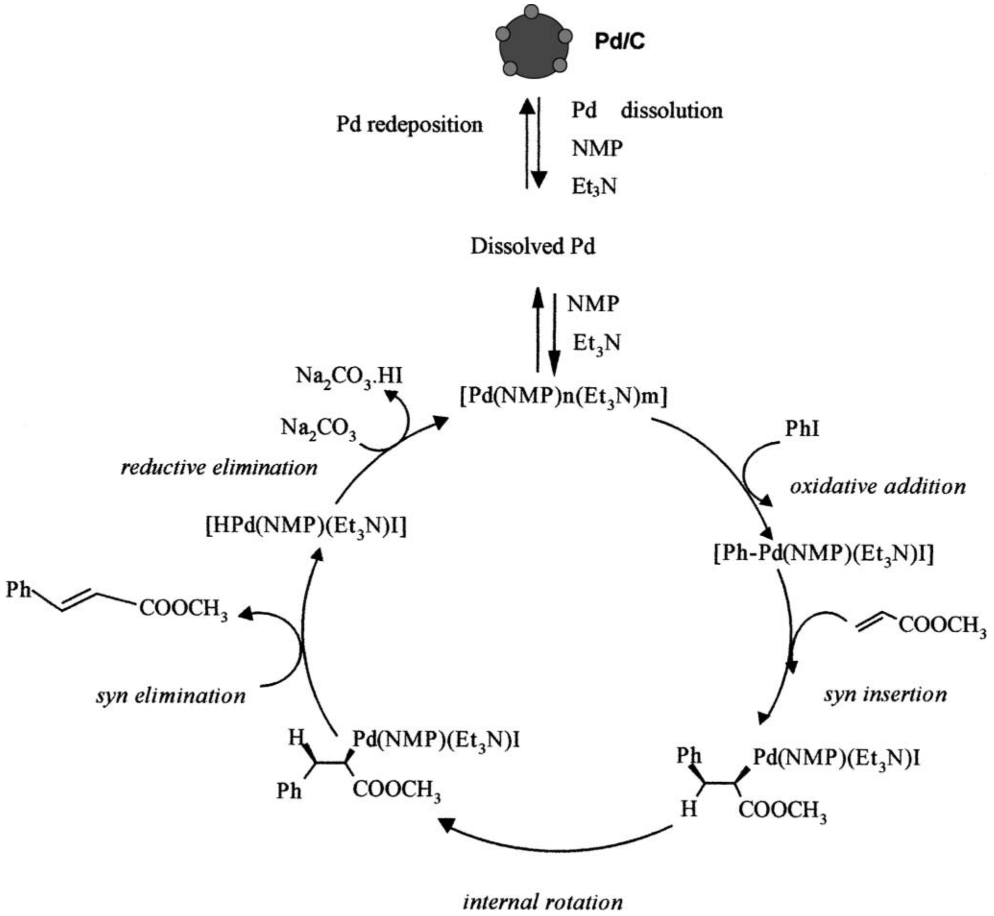


Fig. 4. Bright and dark field TEM images for 10 wt.% Pd/C catalyst before and after Heck vinylation of iodobenzene with methyl acrylate in NMP at 160 °C.



Scheme 3. Mechanism for Heck reaction of iodobenzene and methyl acrylate over a carbon-supported palladium catalyst in NMP in the presence of $Et_3N$ and $Na_2CO_3$ bases.

with NMP and/or $Et_3N$ soluble in the solvent. NMP and/or $Et_3N$ are supposed to be a reducing agent for the formation of palladium(0) species [4].

## 4. Conclusion

The mechanism of palladium leaching and re-deposition has been discussed in this work. The palladium leaching into NMP solvent is caused by the coordination of NMP and/or $Et_3N$ with palladium(0) species, producing catalytically active palladium complexes. These complexes are not stable but react easily with iodobenzene to start the catalytic cycle. Although the reaction mixture is a solid–liquid heterogeneous system, the reaction proceeds homogeneously in the solution and the rate of reaction is comparable to those of originally homogeneous reactions with organopalladium catalysts. When iodobenzene does not exist after its complete consumption, however, palladium of the complexes goes back to the surface of support and it is recyclable for subsequent reactions without loss of activity. The re-deposition of palladium occurs on the surfaces of bare support and/or residual palladium particles depending on the nature of catalyst and the reaction conditions. The mass transfer of leaching and re-deposition results in high reaction rate and in separation and recyclable use of catalyst.

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