

# Heterogeneous catalyst system for Heck reaction using supported ethylene glycol phase Pd/TPPTS catalyst with inorganic base

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## Abstract

A new active Heck vinylation catalyst has been developed using Pd–TPPTS–KOAc (TPPTS: triphenylphosphine trisulfonate sodium salt) immobilized in ethylene glycol film on silica support, which enables easy separation of catalyst as well as base-adduct from reactants/products and it is stable enough for several recycling without the leaching of Pd at high temperatures. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Palladium; TPPTS; Supported liquid phase catalyst; Heck reaction; Catalyst recycling

## 1. Introduction

Heck reaction is an important tool for generating new C–C bonds and it has several applications in synthesis a variety of molecules [1–3]. Considering numerous applications of Heck reactions there is a need for the development of a suitable catalyst/product separation method. Supported aqueous phase catalyst is a well-known method for application of aqueous phase organometallic catalyst using water immiscible substrates [4,5]. Its application at higher temperatures is rather limited mainly due to deterioration of water film. However, a similar concept can be applied using ethylene glycol as catalyst phase [6]. PdCl<sub>2</sub>/TPPTS and Pd(OAc)<sub>2</sub>/TPPTS catalysts (TPPTS: triphenylphosphine trisulfonate sodium salt) are known to work well under aqueous phase intramolecular Heck cyclisation [7] at very high catalyst concentration of 10 mol% of Pd. Tonks et al. [8] have demonstrated application of ethylene glycol film using glass bead technology. They used freeze-dry glass beads coated with ethylene glycol containing Pd/TPPTS catalyst and organic phase containing olefin, aryl halide and triethylamine as organic base. The major drawback of this system is the presence of triethylamine (one of the important catalyst components) in the organic phase. It is known that organic bases like triethylamine have very high affinity for coordination with palladium [9] as compared to inorganic bases like sodium acetate. The organic bases may cause leaching in significant

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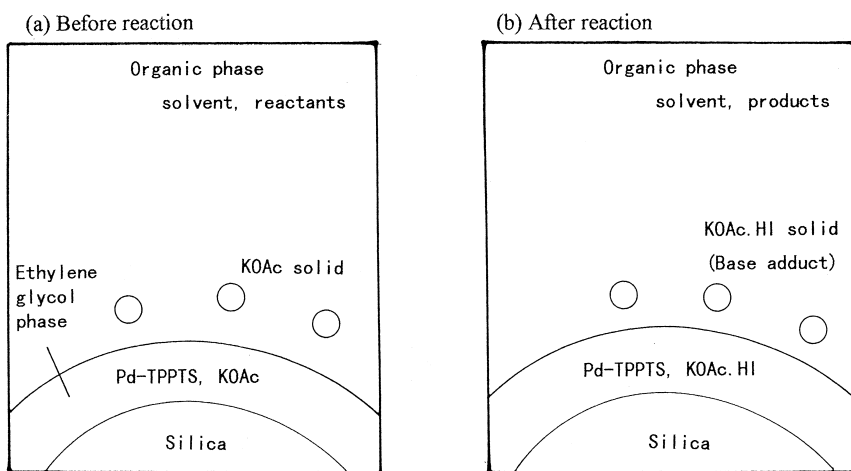
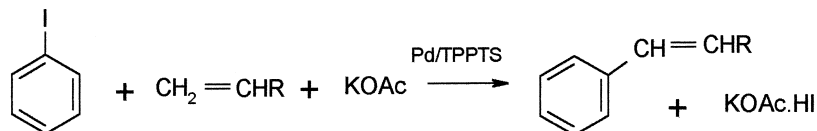


Fig. 1. Schematic illustration of heterogeneous Heck reaction system developed in this work using Pd-TPPTS and an inorganic base of KOAc.

quantities besides the main disadvantage of miscibility with reactants and products. Beller et al. [10] have shown biphasic Heck reaction using Pd/TPPTS catalyst. However, precipitation of Pd metal is a major limitation of the biphasic Pd/TPPTS catalyst system. Li et al. [11] have reported use of metallic Pd supported on porous glass. However, they observed lower conversion and selectivity in many cases and catalyst recycle data were not addressed.

In this work, aiming to overcome the above-mentioned drawbacks with Pd catalysts, a new heterogeneous catalyst system has been developed using Pd-TPPTS immobilized in ethylene glycol film supported on a silica and inorganic base like potassium acetate (Fig. 1). This catalyst has been applied to Heck reactions in organic solvent as follows:



The organic phase (solvent) contains only reactants and products without any catalyst component. It has been shown that the products can easily be separated from the catalyst by simple filtration and the catalyst can be recycled several times without any deactivation. In addition, the present catalyst system can separate not only catalyst but also base-adduct formed during Heck reaction. A new method for regeneration of the catalyst after several recycles has also been developed.

## 2. Experimental

$\text{Pd}(\text{OAc})_2$  (0.1 mmol) and TPPTS (0.2 mmol) were dissolved in 250 mg ethylene glycol under argon atmosphere in a 100 cm<sup>3</sup> round bottom flask agitated with teflon needle. To this solution 1.0 g silica gel (Aldrich Davisil grade 646 35–60 mesh, 300 m<sup>2</sup>/g) and 50 cm<sup>3</sup> toluene were added. This mixture was stirred for 24 h to ensure uniform mixing. Catalyst supported on silica was vacuum dried for 2 h. A typical reaction was conducted as follows. In a mechanical agitated 100 cm<sup>3</sup> autoclave, the

catalyst prepared, iodobenzene (10 mmol), butyl acrylate (20 mmol), KOAc (10 mmol) and toluene (10 cm<sup>3</sup>) were added. The reaction was continued for 20 h at temperatures of 80–130°C, mainly at 120°C. The reaction mixture was filtered and analyzed using GC (Yanaco G3800, Silicone OV-1, 6 m). Conversion based on the amount of iodobenzene reacted was calculated. Leaching of Pd metal catalyst was measured using the atomic absorption spectroscopic method [8]. For recycle studies, residue containing catalyst and base adduct were added instead of fresh catalyst in the above reaction. Regeneration of catalyst is also possible after several recycles. Catalyst containing base adduct was refluxed with 5–10 times excess ethyl acetate. The catalyst transfers into ethyl acetate due to marginal solubility of ethylene glycol in ethyl acetate. Ethyl acetate was evaporated and fresh ethylene glycol and silica were added to the residue and stirred for 4 h in toluene solvent. Then the catalyst was filtered and used for further recycles.

### 3. Results and discussion

The present heterogeneous Heck reaction system prepared is schematically shown in Fig. 1. The overall reaction rate depends on several factors including solvent, inorganic base, catalyst supporting

Table 1  
Heck vinylation of iodobenzene with olefins using supported film catalyst

Catalyst	Base	Olefin	Temperature (°C)	Time (h)	Conversion <sup>a</sup> (%)	Selectivity		Remark
						<i>cis</i>	<i>trans</i>	
<i>Effect of catalyst precursor</i>								
Pd(OAc) <sub>2</sub>	KOAc	Butyl acrylate	120	20	80	–	100	
PdCl <sub>2</sub>	KOAc	Butyl acrylate	120	20	80	–	100	
<i>Effect of base</i>								
Pd(OAc) <sub>2</sub>	Et <sub>3</sub> N	Butyl acrylate	120	20	91	15	85	leaching
Pd(OAc) <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	Butyl acrylate	120	20	10	–	100	
Pd(OAc) <sub>2</sub>	Na <sub>2</sub> CO <sub>3</sub>	Butyl acrylate	120	20	15	–	100	
Pd(OAc) <sub>2</sub>	KOAc	Butyl acrylate	120	20	80	–	100	
Pd(OAc) <sub>2</sub>	NaOAc	Butyl acrylate	120	20	68	–	100	
<i>Effect of temperature</i>								
Pd(OAc) <sub>2</sub>	KOAc	Butyl acrylate	80	24	20	–	100	
Pd(OAc) <sub>2</sub>	KOAc	Butyl acrylate	100	24	35	–	100	
Pd(OAc) <sub>2</sub>	KOAc	Butyl acrylate	120	20	80	–	100	
Pd(OAc) <sub>2</sub>	KOAc	Butyl acrylate	130	10	81	–	100	
<i>Vinylation of various olefins</i>								
Pd(OAc) <sub>2</sub>	KOAc	Methyl acrylate	120	20	75	–	100	
Pd(OAc) <sub>2</sub>	KOAc	Butyl acrylate	120	20	80	–	100	
Pd(OAc) <sub>2</sub>	KOAc	Styrene	120	20	70	10	90	
Pd(OAc) <sub>2</sub>	KOAc	Acrylonitrile	120	20	36	25	75	
Pd(OAc) <sub>2</sub>	KOAc	α-methyl styrene	120	20	38	20	80	
<i>Effect of catalyst supporting film</i>								
Pd(OAc) <sub>2</sub>	KOAc	Butyl acrylate	95	20	15	–	100	H <sub>2</sub> O film
Pd(OAc) <sub>2</sub>	KOAc	Butyl acrylate	95	20	25	–	100	EG film

Iodobenzene: 10 mmol; Olefin: 20 mmol; Base: 10 mmol; Catalyst: 0.1 mmol; TPPTS: 0.2 mmol; Catalyst phase (Ethylene glycol): 250 mg; Silica: 1 g; Toluene (solvent): 10 cm<sup>3</sup>.

<sup>a</sup>Conversion was calculated based on aryl halide consumed.

phase, catalyst precursor and others. We have examined the effects of these factors. The results obtained are summarized in Table 1.

It is observed that the nature of Pd catalyst precursor such as PdCl<sub>2</sub> or Pd(OAc)<sub>2</sub> has no significant effect on catalyst performance and therefore Pd(OAc)<sub>2</sub> was selected for further studies mainly due to its high solubility in ethylene glycol. Several inorganic bases were screened (see Table 1) and KOAc and NaOAc were found to be suitable due to their high solubility in the catalyst containing phase. Potassium carbonate and sodium carbonate are not effective due to poor solubility in the ethylene glycol. We confirmed no leaching of Pd metal up to 0.1 ppm level. An organic base of triethylamine was found to be effective. However, it has two major drawbacks: very high leaching of Pd in the organic phase due to its high affinity towards Pd and miscibility with the reactants and products. Inorganic base such as sodium acetate is known to give acetic acid and sodium bromide in the case of aryl bromide and butyl acrylate vinylation [12] in *N,N*-dimethyl acetamide. In the present catalyst system we observed the formation of a base adduct (KOAc.HI) [13] instead of acetic acid and sodium iodide. This is needed for the present catalyst system, since formation of acetic acid will leach out catalyst in the organic phase. KOAc can be added during the catalyst preparation stage or during the course of reaction and this does not cause any effect on reaction profile. It is essentially dissolved in catalyst phase and reaction occurs only in the catalyst film. Product is delivered to toluene (solvent) due to its high solubility in toluene whereas base adduct is not soluble in toluene and is separated as solid in the reaction mixture (Fig. 1). Several solvents such as chloroform, methylene chloride, hexane, octane and xylene were also screened. Chloro solvent was found to deactivate the catalyst rapidly by formation of Pd metal particles. Aliphatic solvents were not found suitable for higher temperature. Aromatic solvents such as toluene and xylene give good results and therefore toluene was selected in this work. Effect of catalyst film was also screened and it has been observed that ethylene glycol is more active than water film. Water film has another disadvantage as it deteriorates at high temperatures as 120–140°C. The catalyst is active for almost all types of olefins as indicated in olefin screening studies in Table 1. Effect of different aryl halides has also been studied under conditions given in Table 1. Very low conversion (28%) was observed in the case of bromobenzene and no reaction occurred with chlorobenzene as a substrate. Currently it is a challenging task to develop an active catalyst for Heck reaction with chlorobenzene, which is a cheaper substrate than iodobenzene.

For effective utilization of catalyst it is necessary that it can be recycled several times. Results on catalyst recycling are presented in Table 2. It can be seen that the reaction proceeds very fast in the first 8 h with 44% conversion. The catalyst was filtered along with base adduct and recycled for next reaction with freshly added KOAc, butyl acrylate and iodobenzene. The catalyst retains its activity and selectivity performance even up to five recycles. We stopped recycle experiments after five recycles. In Set B, KOAc was not added in further recycle to assess the catalytic nature of base or base adduct. Beller and Riermeier [9] indicated that base can act in understoichiometric amount. They observed that 0.6 equivalent of base (triethylamine) gives 80% conversion. In recycle 2 (set B) 40% conversion was obtained due to unreacted KOAc present from earlier reaction. Recycle data for reactions 3, 4, 5 (set B) indicated 16% conversion without addition of fresh base. The nature of catalyst cycle during this is not clear. After several recycles catalyst, containing base adduct, can be separated by extraction in ethyl acetate (see Section 2). This catalyst (Table 1, recycle 6) is also active for Heck vinylation and can be further recycled several times. TON of our catalyst system is more than 200 (mol product/mol Pd) per recycle. The catalyst is active for more than 1200 TON without deactivation. Higher TON reported by Herrmann et al. [12] using palladocycles as a catalyst are in the range of 5000–20,000 and applicable only in the case of activated aryl bromides. Normal aryl

Table 2  
Catalyst recycle for Heck vinylation of butyl acrylate and iodobenzene

Recycle number	Time (h)	ArI consumed (mmol)	Butyl acrylate consumed (mmol)	Conversion (%)	Selectivity to trans (%)
<i>Set A: KOAc added in each recycle</i>					
1	0	0	0	0	100
	4	7.8	7.8	26	100
	8	13.2	13.3	44	100
	20	22.1	22.1	80	100
2	20	22.2	22.2	74	100
3	20	21.8	21.9	72.6	100
4	20	21.7	21.9	72.3	100
5	20	21.7	21.8	72.3	100
6 (regen)	40	25.2	25.2	84	100
<i>Set B: KOAc was not added during recycle</i>					
1	20	22.1	22.1	80	100
2	20	12.1	12.4	40.3	100
3	20	4.8	4.9	16	100
4	20	4.8	4.9	16	100
5	20	4.8	4.9	16	100

Iodobenzene: 30 mmol; Butyl acrylate: 60 mmol; KOAc: 30 mmol; Catalyst: 0.1 mmol; TPPTS: 0.2 mmol; Ethylene glycol: 250 mg; Silica: 1 g; Toluene (solvent): 10 cm<sup>3</sup>; Temperature: 120°C.

bromide gives TON in the range of 50–800 using palladocycle catalyst. Separation of salt formed during reaction is the disadvantage of this catalyst system as it remains with reactants and products.

#### 4. Conclusion

The present catalyst system comprising of Pd/TPPTS catalyst in ethylene glycol film supported on high surface area silica along with inorganic base such as KOAc is effective for heterogenizing the Heck reaction. The activity of this catalyst is comparable to the active homogeneous catalysts reported in the literature. Our catalyst system has such advantages that the separation of product from the catalyst is very easy and its recycle efficiency is also very high.

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