

Heck reaction with a silica-supported Pd-TPPTS liquid phase catalyst: effects of reaction conditions and various amines on the reaction rate

Shin-ichiro Fujita*, Takeshi Yoshida, Bhalchandra M. Bhanage, Masahiko Arai

Division of Materials Science and Engineering, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan

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Abstract

Supported liquid phase catalysts (SLPC) were prepared using a porous silica, ethylene glycol (EG), and triphenylphosphine trisulfonate sodium salt (TPPTS) and used for the Heck reaction of iodobenzene (PhI) and butyl acrylate (BA) in the presence of amine. The reaction rate depends on the concentration of Pd-TPPTS complex in the supported EG phase, not on the total quantity of Pd-TPPTS. The rate increases linearly with the PhI concentration. The reaction rate also increases linearly with the concentrations of BA and triethylamine (Et_3N) when these are low. However, a plateau and a maximum of the rate are seen with further increasing the concentrations of BA and Et_3N , respectively. As a result of the complex of these modes of the dependence, the reaction rate increases with the total concentration of PhI, BA and Et_3N in an order of two. The dependence of the reaction rate on those concentrations with a palladium-triphenylphosphine (Pd-TPP) homogeneous catalyst is quite similar to that with SLPC. The reaction rate depends also on the type of the amine used. Tributylamine (Bu_3N) gives faster reaction rates than Et_3N with both SLPC and Pd-TPP. However, such an effect of trihexylamine (Hex_3N) is seen only with Pd-TPP. In the SLPC system, Hex_3N gives almost the same rate as that with Et_3N . Promotive effect of recycle use of the SLPC sample is also affected by the type of the amine.

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1. Introduction

Organometallic complexes are excellent catalysts for various chemical transformations, since their activity and selectivity are optimized by judicious choice of metallic elements and organic ligands [1]. However, these catalysts have a drawback to the catalyst separation and recycle. One of the methods overcoming this drawback is using supported liquid phase cat-

alyst (SLPC), in which thin liquid film containing organometallic complexes is supported on the surface of high-surface area solid [2–4]. The SLPC is used in a solvent that does not dissolve the film liquid and can be easily separated by simple filtration and recyclable. The idea of the SLPC was proposed by Davis and co-workers [3]. They prepared a thin aqueous phase containing rhodium complexes over the surface of a porous silica and its good performance was proven for hydroformylation, as reviewed by Davis [4].

Heck reaction of aryl halide with olefins is one of the reactions for the formation of new C–C bonds, and important from practical and scientific points of view

* Corresponding author. Tel.: +81-11-706-6596;
fax: +81-11-706-6594.
E-mail address: sfuji@proc-ms.eng.hokudai.ac.jp (S.-i. Fujita).

[1,2,5–8]. In the literature, there are several works using SLPC with different metal complexes, liquid films, and supporting materials for Heck reactions [2,9–15]. However, little attention has been paid to kinetics of the reaction, although the reaction mechanism was proposed [5–8]. To our knowledge, there are only two reports in which the kinetics of Heck reaction has been studied with a homogeneous catalyst [16] and with palladocycle catalysts [17]. No one has reported such a study for SLPC. In the present study, Heck reaction of iodobenzene (PhI) and butyl acrylate (BA) in the presence of amine ($\text{PhI} + \text{C}_2\text{H}_3\text{COOC}_4\text{H}_9 + \text{R}_3\text{N} \rightarrow \text{PhC}_2\text{H}_2\text{COOC}_4\text{H}_9 + \text{R}_3\text{NHI}$) using SLPC has been carried out. Effects of catalyst preparation conditions, the concentrations of the substrates and the amine on the reaction rate were studied. For comparison, the reaction in a homogeneous system was also investigated.

2. Experimental

2.1. Catalyst preparation

SLPC samples containing Pd-triphenylphosphine trisulfonic acid trisodium salt (TPPTS) were prepared using ethylene glycol (EG) as a dispersed phase and a porous silica gel (Aldrich DAVISIL grade 646), which has a BET surface area of $294 \text{ m}^2/\text{g}$, an average pore diameter of 20 nm, and a total pore volume of about 1 ml. EG, palladium acetate and TPPTS were added into a 200 ml glass reactor and mixed at 60–70 °C to prepare Pd-TPPTS complexes. The formation of the palladium complex was ascertained from change in color to dark brown. Then silica gel was added and further mixed for several minutes and 40 ml of toluene was added. The suspension was stirred at room temperature in order for the EG phase to disperse well on the surface of silica gel. The ratio of TPPTS/Pd was fixed to two for all the SLPC samples prepared.

Palladium-triphenylphosphine (Pd-TPP) homogeneous catalyst was prepared in toluene from palladium acetate and TPP. The quantities of palladium acetate and the ligand were fixed to 0.2 and 0.4 mmol, respectively, and that of toluene was the same as that for SLPC.

2.2. Heck reaction

After the preparation of SLPC, the glass reactor with a condenser and a mechanical agitator was heated

to a reaction temperature of 100 °C. Then in a typical experiment, 20 mmol of PhI, 40 mmol of BA and 20 mmol of triethylamine (Et_3N) were added to start the Heck reaction. The reaction runs were carried out under ambient atmosphere for 1 h. A portion of the reaction mixture was repeatedly taken out from the reactor and it was analyzed by a capillary gas chromatograph with flame ionization detector. In some experiments, the concentrations of the substrates and the amine were changed and tributylamine (Bu_3N) or trihexylamine (Hex_3N) was used instead of Et_3N . It is noted that the conversion of PhI was always below 10% under the reaction conditions employed, allowing us to measure the reaction rate.

For comparison, experiments with the Pd-TPP homogeneous catalyst were carried out. Procedures following the catalyst preparation and reaction conditions were similar to those with SLPC.

Recycle use of the SLPC was also conducted. After a reaction run, the catalyst was separated by filtration and rinsed with toluene several times. Then the catalyst was reused for a subsequent run in which the desired amounts of fresh toluene, the substrates and the amine were used.

3. Results and discussion

Under the reaction conditions employed in the present study, butyl cinnamate was selectively produced as the only product. Fig. 1 illustrates a typical variation of the product concentration with time. The product concentration increases linearly with time after a short induction period. Such an induction period was reproducibly observed using as-prepared SLPC samples. The reaction rate was determined from the slope of the data within the steady state region.

3.1. Effects of reaction conditions

The reaction was carried out with changing the amount of EG where the concentration of palladium acetate was fixed at constant values. As Fig. 2 shows, the reaction rate little changes with the amount of EG used but it depends on the Pd-TPPTS concentration in the film. BET surface areas of the SLPC samples on which various amounts of EG were supported were measured. It was found that the BET surface area did

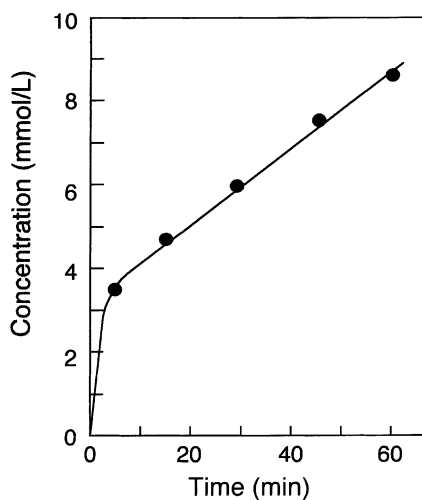


Fig. 1. Typical variation of the product concentration with time. Reaction conditions: PhI, 20 mmol; BA, 40 mmol; Et₃N, 20 mmol; toluene, 40 ml; temperature, 100 °C. Catalyst: palladium acetate, 0.2 mmol; TPPTS, 0.4 mmol; EG, 1.0 g; silica, 2.0 g.

not change with the amount of EG supported and was practically the same as that of bare silica. This suggested that EG disperses uniformly on the surface of silica and only the thickness of the supported EG film changes with its amount. Hence, it is highly probable that the reaction proceeds at the interface between the supported EG film and the solvent of toluene.

Effects of the concentrations of PhI, BA and Et₃N upon the reaction rate were investigated. Fig. 3a shows

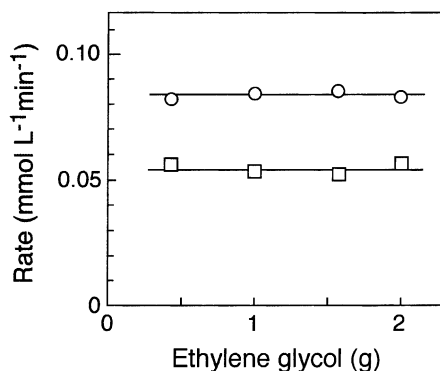
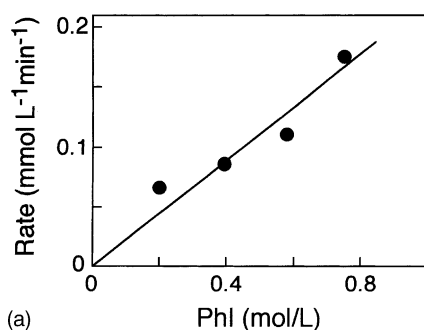
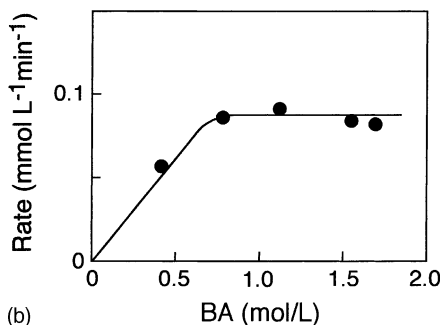


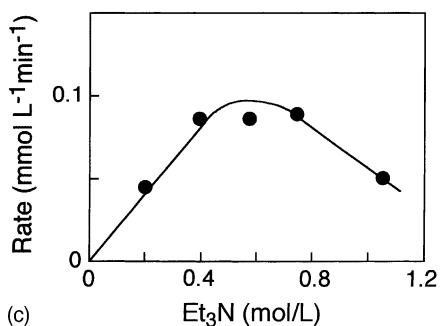
Fig. 2. Effects of the quantity of EG at constant concentrations of Pd-TPPTS. The concentrations of Pd-TPPTS were (□) 0.1 and (○) 0.2 mmol/g of EG. The reaction conditions and the quantity of silica were the same as given in Fig. 1.



(a)



(b)



(c)

Fig. 3. Effects of the concentrations of (a) PhI, (b) BA and (c) Et₃N upon the reaction rate with SLPC. One of these concentrations was changed with keeping the others concentrations constant. The standard concentrations and the reaction conditions were the same as given in Fig. 1.

the effect of the PhI concentration upon the reaction rate. The reaction rate is proportional to the concentration of PhI. The dependence of the reaction rate upon the concentration of BA or Et₃N is different from that on the PhI concentration. As Fig. 3b shows, the reaction rate increases proportionally in a lower region of the BA concentration and the reaction rate is practically constant above 0.8 mol/l. When the concentration

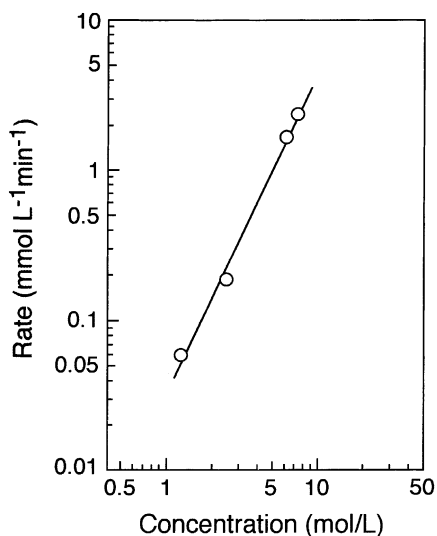


Fig. 4. Relationship between the reaction rate with SLPC and the concentration of a mixture of PhI, BA and Et₃N (1:1:1). The reaction conditions and the quantity of SLPC were the same as given in Fig. 1 except the concentrations of the substrates and the amine.

of Et₃N is varied, the reaction rate passes through a maximum around 0.6 mol/l (Fig. 3c). Thus, an excessive amount of Et₃N retards the reaction.

For practical usage of the Heck reaction, it should be also important to know effects of the total concentration of the substrates and the amine. Fig. 4 shows the dependence of the reaction rate with SLPC on the concentration of a mixture of PhI, BA and Et₃N whose ratio is 1:1:1. The highest concentration of the mixture examined corresponds to the neat reaction. The reaction rate increases with the concentration of the mixture in an order of two. Even at the higher mixture concentrations, butyl cinnamate was selectively formed. Compounds that can be produced via the successive reaction of butyl cinnamate and PhI were not detected.

For comparison, several experiments were carried out with the Pd-TPP homogeneous catalyst. The results obtained are illustrated in Figs. 5 and 6. Although the reaction rate with Pd-TPP is much faster than that with SLPC, its dependence on the concentration of PhI, BA or Et₃N is very similar to that obtained with SLPC. The rate increases linearly with the PhI concentration (Fig. 5a), and a plateau and a maximum of

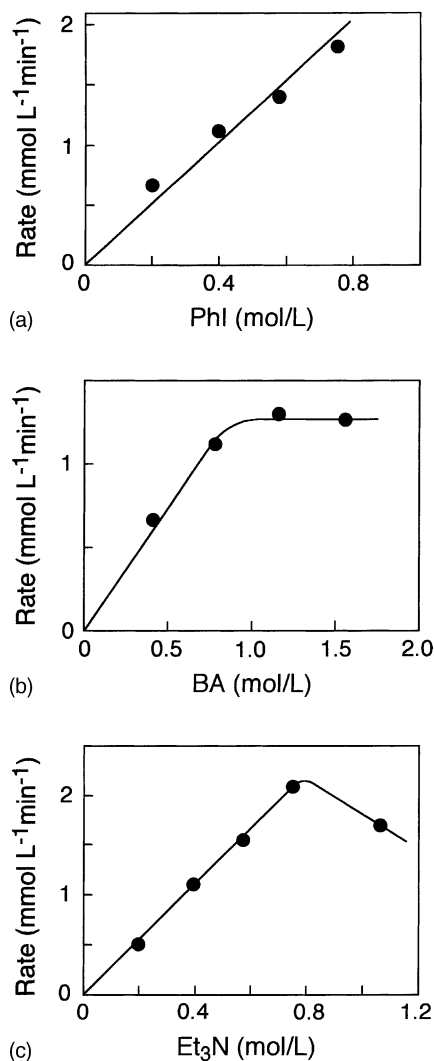


Fig. 5. Effects of the concentrations of (a) PhI, (b) BA and (c) Et₃N upon the reaction rate with Pd-TPP homogeneous catalyst. One of these concentrations was changed with keeping the others concentrations constant. The standard concentrations and the reaction temperature were the same as given in Fig. 1. The quantity of Pd-TPP was 0.2 mmol.

the rate are seen with varying the concentrations of BA and Et₃N, respectively (Fig. 5b and c). The Et₃N concentration where the maximum appears is slightly higher in the homogeneous system than in the SLPC system. Similar results have been reported for the reaction of PhI and methyl acrylate with Pd-TPP [16]. As Fig. 6 shows, the dependence of the reaction rate

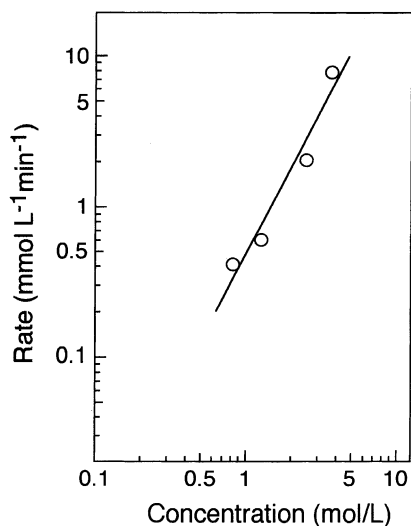


Fig. 6. Relationship between the reaction rate with Pd-TPP and the concentration of a mixture of PhI, BA and Et₃N (1:1:1). The reaction conditions and the quantity of Pd-TPP were the same as given in Fig. 5 except the concentrations of the substrates and the amine.

on the total concentration of the PhI, BA and Et₃N mixture is the same as that with SLPC. Thus, the kinetics of the reaction is very similar in both SLPC and homogeneous systems. It seems that the Heck reaction with SLPC is little affected by diffusion of the substrates and the amine on the surface and in the pore of silica.

As discussed previously [16], the results shown in Figs. 3 and 5 can be explained on the basis of the mechanism of Heck reaction. Fig. 7 illustrates an well-accepted scheme for the reaction mechanism. The reaction is initiated by the oxidative addition of PhI to the palladium(0) complex **1**, generating σ -aryl palladium(II) complex **2**. As the concentration of PhI increases, more amount of σ -aryl palladium(II) complex **2** are formed, resulting in the linear dependence of the reaction rate on the PhI concentration. Addition of olefin to the aryl complex **2** leads to the formation of π -complex, transforming to σ -complex **3**. Since the formation of π -complex is an equilibrium reaction [5,8], its reverse reaction would be enhanced at higher concentrations of olefin. Hence, the overall reaction rate is marginally dependent on the olefin concentration in its higher region. The complex **5** is regenerated to the palladium(0) complex **1** via the reductive elimination of HI. When the amine concentration is excessively high, it might coordinate to at least one of the palladium complexes, resulting in the decrease in the concentration of the active catalyst species. Amatore and Jutand [18] showed that the oxidative addition of PhI to an anionic palladium(0) complex was decelerated by amine. This decelerating effect of amine might be also taken into account. Thus, the maximum of the reaction rate appears with increasing the amine concentration. The results shown in Figs. 4 and 6 are difficult to explain. Probably, these should arise from the composite effects of the individual concentrations

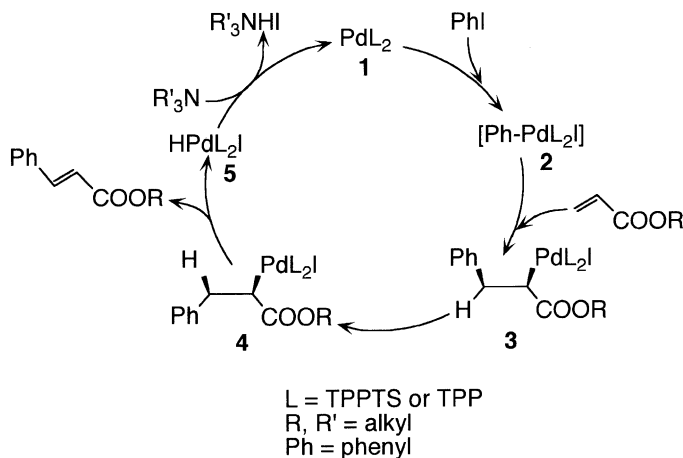


Fig. 7. A scheme for the mechanism of Heck reaction.

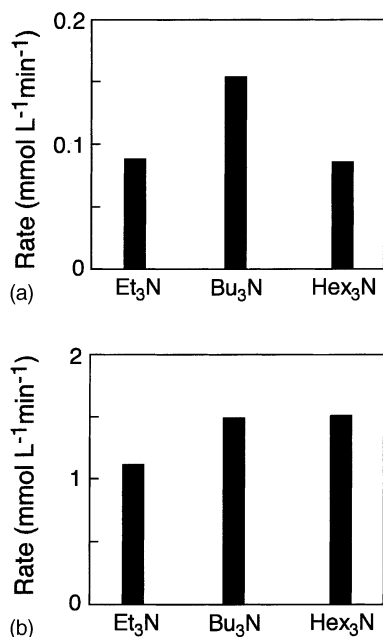


Fig. 8. Effect of the type of the amine used for the reaction with (a) SLPC and (b) Pd-TPP homogeneous catalyst. Et_3N , Bu_3N and Hex_3N represent triethylamine, tributylamine and trihexylamine, respectively. The reaction conditions and the quantities of the catalysts were the same as given in Fig. 1.

of the substrates and the amine upon the reaction rate.

3.2. Effect of types of amines

Fig. 8 depicts the effect of the type of the amine used for the reaction with the SLPC and homogeneous catalysts. With both the catalysts, when Bu_3N is used for the reaction instead of Et_3N , the reaction rate is enhanced. On the other hand, when Hex_3N is used, such an enhancement is not observed with the SLPC catalyst, whereas the reaction rate with the homogeneous catalyst increases. This difference between the SLPC and Pd-TPP catalysts for the reaction with Hex_3N could result from lower affinity of Hex_3N for EG. If the amine acts merely as a neutralizer for HI co-generated in the solvent, the type of the amine should have little effect on the reaction rate. Hence, the amine should take part in the course of the reductive elimination of HI from the palladium complex **5** by interacting with or coordinating to the complex.

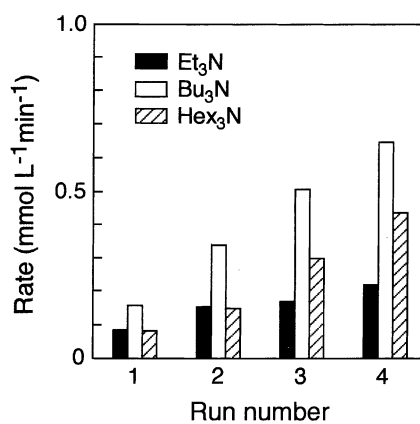


Fig. 9. Change of the reaction rate on the recycling of SLPC in the presence of Et_3N , Bu_3N and Hex_3N as the base. Et_3N , Bu_3N and Hex_3N represent triethylamine, tributylamine and trihexylamine, respectively. The reaction conditions and the quantity of SLPC were the same as given in Fig. 1.

The present authors previously reported that the recycle use of a SLPC sample enhances its catalytic activity [15]. The type of the amine also affects the extent of the enhancement. Fig. 9 shows the reaction rates collected with SLPC samples for several repeated runs by using Et_3N , Bu_3N or Hex_3N as the base. The reaction rate increases by the reuses irrespective of the type of the amine and the highest reaction rate is always obtained with Bu_3N in each successive recycle. However, the extent of the increase in the reaction rate, i.e. the ratio of the reaction rate of the repeated run against that of the first run, is largest with Hex_3N , when it is plotted against the amount of trialkylammonium iodide formed during the reaction (Fig. 10). The present authors previously reported that adding triethylammonium iodide (Et_3NHI) to the EG phase in the course of the catalyst preparation also causes the enhancement of the reaction rate [15]. The extent of the enhancement was found to be similarly correlated with the amount of Et_3NHI formed during the reaction and the amount added to the EG phase. Hence, it has been concluded that the enhancement by the reuse of SLPC results from the formation and accumulation of Et_3NHI in the EG phase [15]. Addition of Et_3NHI also enhances the catalytic activity even in the homogeneous system. When the reaction was carried out with adding 2 mmol of Et_3NHI into

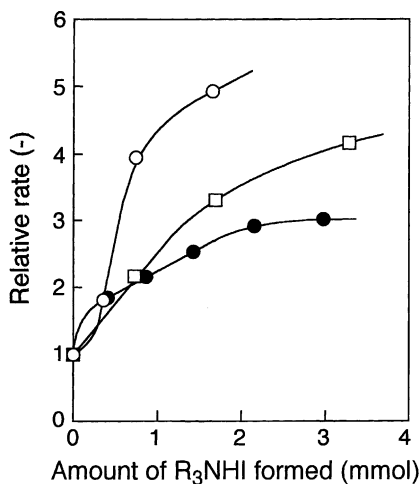


Fig. 10. Relationships between the relative rate of the reaction and the total amounts of (●) Et₃NHI, (□) tributylammonium iodide and (○) trihexylammonium iodide formed in the course of the reaction. The reaction conditions and the quantity of SLPC were the same as given in Fig. 1.

the solvent of toluene, the reaction rate obtained was 1.7 times as fast as that obtained without the addition of Et₃NHI. Previously, Jeffery reported promotive effects of tetraalkylammonium salts on a Heck reaction with Et₃N as the base in a homogeneous system [19]. He proposed that the ammonium salts directly interact with the complex **5** through hydrogen bonding and promote the regeneration of the complex **1**. Probably, a similar process should proceed in the course of the reaction with the recycled SLPC catalyst, resulting in the enhancement of the activity. The strength of the hydrogen bonding might depend on the carbon chain length of the amine and hence the extent of the enhancement would change by the type of the amine used.

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