



Heck reactions with various types of palladium complex catalysts: application of multiphase catalysis and supercritical carbon dioxide

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Abstract

The application of multiphase catalytic systems for palladium catalyzed Heck reactions brings several benefits such as easy catalyst–product separation and catalyst recycling. The effective multiphase Heck systems can be prepared by using different types of catalyst phases, including biphasic catalysis and supported liquid phase catalysts, and a new generation solvent of supercritical carbon dioxide.

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Keywords: Heck reaction; Biphasic catalysis; Supported liquid phase catalyst; Supercritical carbon dioxide

1. Introduction

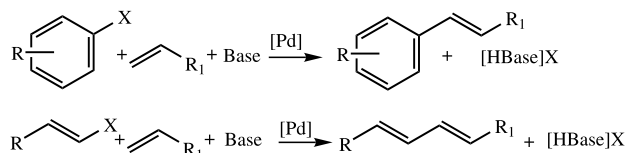
Heck reaction has gained considerable interest in recent years as one of the important tools for C–C bond formation [1–4]. This reaction produces coupling products from olefins and halides. It has been used for the synthesis of several intermediates in pharmaceutical and fine chemicals. For example, the synthesis of taxol, one of active anticancer drugs, involves an intramolecular Heck reaction [5]. Substituted cinnamic acids and corresponding esters, which find extensive applications as ultraviolet absorbers as well as antioxidants, are also synthesized via Heck reactions [6,7]. Bromine Compounds Ltd. has developed a new process for the synthesis of *p*-methoxycinnamic acid 2-ethyl hexyl ester via *p*-bromoanisole and acrylic acid [8]. Hoechst AG has developed an industrial process for the synthesis of 6-methoxy-2-vinylnaphthalene starting from ethylene and 6-methoxy-2-bromonaphthalene [4,9]. The reaction is normally carried out using a soluble Pd catalyst with a phosphine ligand and a base in a homogeneous medium (Scheme 1).

The most frequently used catalysts for Heck reactions are complexes derived from palladium salts and phos-

phine ligands. The phosphine ligands are necessary to stabilize the palladium catalyst; otherwise, the metal will precipitate. Organic and/or inorganic bases are used for regeneration of the catalyst by eliminating HX and leaving the active Pd complex in the final stage of the catalytic cycle according to a well-established mechanism [3,10]. The rates of homogeneous Heck reactions catalyzed with palladium complexes are sufficiently high; for their potential applications, however, they suffer from a major drawback in the catalyst–product separation and in the catalyst recycling. It is often undesirable to lose palladium even at ppm levels because of its significantly high cost. In such cases, the catalyst–product separation strategies are very important for industrial applications of Heck reactions. The present article will review our recent works on multiphase Heck reactions using various types of palladium catalysts, including biphasic catalysis, supported liquid phase catalysts, and homogeneous catalysis. Kinetics of a homogeneous Heck reaction, catalyst separation strategies, and usefulness of a new generation solvent of supercritical carbon dioxide have been described. Although the concepts described in this article are shown for Heck reactions, they are of wide applicability to other homogeneously catalyzed reactions of practical significance, such as hydrogenation, carbonylation, hydroformylation, and so on. The concepts may be

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X = I, Br, Cl, N₂BF₄, CF₃SO₃, Base = NR₃, K₂CO₃, KOAc, NaOAc

Scheme 1. Heck coupling reaction.

helpful for reducing the use and emission of undesired hazardous materials and thus developing green chemistry processes.

2. Homogeneous Heck reactions

Heck reactions using homogeneous palladium catalysts have widely been studied and several informative reviews describing the state of the art along with the reaction mechanism are available [1–4]. The kinetics study for Heck reactions was lacking and very few efforts have been made on this aspect. It is important to know the influence of various reaction parameters on the reaction rate. We have recently reported a detailed kinetic study for a homogenous Heck coupling of iodobenzene and methyl acrylate in the presence of triethylamine as a base [11]. The reaction rate shows linear dependence on the iodobenzene concentration. The reaction rate increases linearly in a lower region of methyl acrylate concentration and marginally increases afterwards. The effect of triethylamine concentration passes through a maximum and excessive amount of triethylamine retards the reaction. These results are qualitatively explained on the basis of the well-accepted Heck reaction mechanism. The influence of catalyst and ligand (triphenylphosphine) concentrations was also investigated. It was difficult to obtain a rate expression according to the reaction mechanism but an empirical expression, which well fits the kinetics data, was proposed as follows. The apparent activation energy was found to be 23 kcal/mol from the data at 50, 60, and 70 °C.

$$\text{Rate} = \frac{kAB^2CD}{(1 + K_B B^2)(1 + K_C C^4)(1 + K_D D)^3(1 + K_E E)}$$

where k = rate constant; A = iodobenzene concentration; B = olefin concentration; C = base concentration; D = catalyst concentration; E = ligand concentration and K_B , K_C , K_D and K_E are constants.

We have also studied the effect of the palladium/ligand ratio on the reaction rate in various solvents for the same reaction [12]. The reaction rates obtained in polar solvents such as *N*-methylpyrrolidone and *N,N'*-dimethylacetamide are very high as compared with those obtained in less-polar solvents such as ethanol,

toluene and octane. In the polar solvents, the reaction rate shows significant drop with increase in the ratio, whereas in the less-polar solvents it passes through a maximum at a palladium–ligand ratio of 2 and the precipitation of palladium metal was observed in the absence of the ligand. Such a metal precipitation was not observed in the polar solvents. Similar results were obtained with an inorganic base of potassium acetate instead of triethylamine. It has been proposed that active species produced in the polar solvents involves the solvent molecules.

3. Biphasic Heck reactions

It is well-known that homogeneous catalysts consisting of soluble metal complexes have high activity and selectivity as compared with heterogeneous catalysts. In spite of this, their applications in industry are limited due to difficulty in the catalysts–product separation and in the catalyst recycling. Catalysis in liquid–liquid two phases is generally referred as biphasic catalysis and has widened the scope of homogeneous catalysis in practice [13]. The catalyst is present in one phase (water in many cases) while reactants and products are present in the other organic phase. Thus the catalyst can be separated by simple phase separation. A most frequently used ligand for the water-soluble complexes is triphenylphosphine trisulfonate sodium salt (TPPTS). The easy catalyst separation is an important step towards the development of environmentally friendly processes. Hoechst AG is operating a 300,000 tons per annum plant for hydroformylation of propylene using Rh and a water-soluble phosphine complex in a biphasic mode of operation. Prof. Genet has reviewed Pd catalyzed reactions in aqueous medium [14].

We have studied a toluene–ethylene glycol biphasic catalytic system for a Heck vinylation reaction of iodobenzene and butyl acrylate in the presence of potassium acetate (Fig. 1) [15]. The activity, selectivity, stability and recycling performance of various catalysts, which include Pd, Pt, Rh, Ni and Co based catalysts,

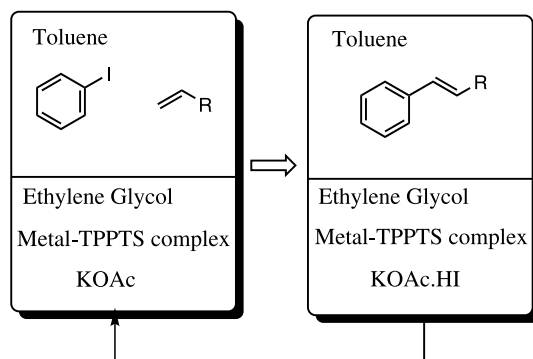


Fig. 1. A biphasic catalyst system for Heck reaction.

Table 1
Liquid–liquid biphasic Heck vinylation of iodobenzene with butyl acrylate using various metal–TPPTS catalysts

Run no.	Catalyst precursor	Metal:TPPTS ratio	Conversion (%)	Selectivity (%)	
				BC	Benzene
1	Pd(OAc) ₃	2	100	100	0
2	PdCl ₂	2	99	100	0
3	Pd(OAc) ₂	4	100	100	0
4	Ni(OAc) ₂	2	74	98.6	0.4
5	Rh(CO) ₂ (acac)	2	30	0	100
6	RhCl ₃	3	60	0	100
7	RuCl ₃	3	71	98.7	0.3
8	Pt(COD)Cl ₂	2	59	85.8	14.2
9	CoCl ₂	2	63	90.2	9.8

Butyl acrylate: 10 mmol; Iodobenzene: 10 mmol; KOAc: 10 mmol; catalyst precursor: 0.1 mmol; temperature: 140 °C; ethylene glycol: 10 cm³; toluene: 10 cm³; reaction time: 12 h; BC: butyl cinnamate; acac: acetylacetonato; COD: 1,5-cyclooctadiene. Conversion was calculated based on the amount of iodobenzene consumed.

have been investigated in detail. As shown in Table 1, the performance of Pd based catalyst is far superior, although other cheaper catalysts are also active. The catalyst phase can be separated by simple phase separation and recycled more than three times retaining its activity and selectivity performance. The base adduct can be separated as a solid precipitation after the concentration of the base adduct in the ethylene glycol phase has saturated after repeated runs. An additional advantage of potassium acetate as a base is that it keeps the concentration of palladium leaching into the organic phase to very low levels.

4. Supported aqueous phase catalysts for Heck reactions

Davis et al. proposed supported aqueous phase catalyst (SAPC) [16,17], in which aqueous thin film containing water soluble organometallic complexes is supported on hydrophilic high surface area solid such as silica. The SAPC is used in a solvent immiscible with the film liquid and can be easily separated by simple filtration. Water-soluble solvents like ethylene glycol can also be used as a film liquid. In such cases, the catalyst may be called supported liquid phase catalyst (SLPC). Another advantage of SAPC is that SAPC has a high liquid–liquid interfacial area arisen from the high surface area of the support, since, in the biphasic system, overall reaction rate is sometimes limited by its low liquid–liquid interfacial area and it is difficult to increase this area by mechanical agitation [18]. The concept of SAPC is well proven in the case of hydroformylation reaction [16,17]. We used supported ethylene glycol phase Pd–TPPTS catalyst (Pd–SLPC) [19] and Ni–TPPTS catalyst (Ni–SLPC) [20] for Heck reactions in the presence of inorganic base. Pd–SLPC is superior as compared with Ni–SLPC with respect to

the catalyst stability and activity. Ni–SLPC was found to deactivate during successive uses.

The influence of catalyst preparation variables for Pd–SLPC has also been studied in detail [21,22]. The substrates were iodobenzene and butyl acrylate and the base was triethylamine (Fig. 2). The reaction rate depends on the concentration of Pd–TPPTS complex in the ethylene glycol phase dispersed on silica but not on the total quantity of Pd–TPPTS complex. This suggests that the ethylene glycol film dispersed uniformly on the support and the reaction takes place at the interface between the film and the solvent. Interestingly, the reaction rate is enhanced on recycling of the catalyst as shown in Fig. 3. Probably, triethylammonium iodide salt, which is formed in the course of the Heck reaction and accumulated on the SLPC, should promote the reaction. Promotional effect of triethylammonium iodide was also observed in the homogeneous reaction [22] and Jeffery had reported such effect of tetraalkylammonium salts in homogeneous Heck reactions [23].

The dependence of the reaction rate on the concentrations of the substrates or the amine was quite similar to that obtained with Pd–TPP homogeneous catalyst described above. It was also found that both the

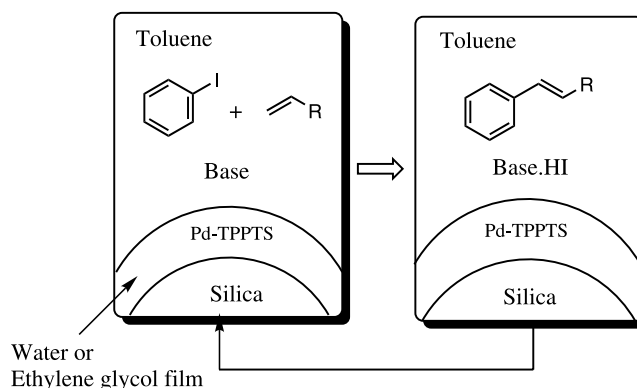


Fig. 2. A multiphase Heck reaction system using SLPC.

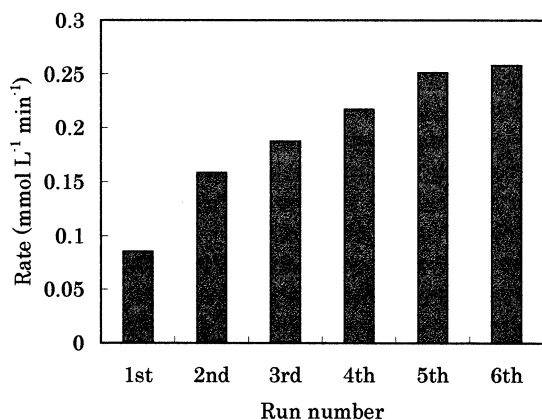


Fig. 3. The change of the rate of Heck reaction on the recycling of SPLC sample in the presence of triethylamine as a base. Catalyst: palladium acetate 0.2 mmol, TPPTS 0.4 mmol, ethylene glycol 1.0 g, silica gel 2.0 g. Reaction conditions: iodobenzene 20 mmol, butyl acrylate 40 mmol, base 20 mmol, toluene 40 ml, temperature 100 °C.

reaction rates obtained with Pd–SLPC and Pd–TPP increase with the total concentration of the substrates and the amine in an order of two. These results suggested that the Heck reaction with SLPC is little affected by diffusion of the substrates and the amine in the solvent and in the pore of silica. The reaction rate also depended on the type of the amine used. Tributylamine gave faster reaction rates than triethylamine for both Pd–SLPC and Pd–TPP homogeneous catalyst. For trihexylamine, however, such an effect was seen only with Pd–TPP. In the SLPC system, trihexylamine gave almost the same rate as that with triethylamine. The type of the amine used also affected the enhancement in the reaction rate on catalyst recycling.

5. Multifunctional catalysis with SLPC

The chemical synthesis of variety of compounds often passes through several reaction sequences. It is desirable to use a multifunctional catalyst system for eliminating some of these steps and producing economical benefit. However, this would not be an easy problem to solve using homogeneous organometallic catalysts, since coordination chemistry of each metal is quite different. Usually, when two or more homogeneous organometallic catalysts are mixed together, they would lower their respective performance by some negative interactions. Besides the advantage in the catalyst separation, the SLPC technique may contribute to the design of multifunctional catalytic systems. Because, when a mixture of two or more different SLPC samples are used in a single reaction system, they may remain being separated by the solvent and hence the interaction between the metal complexes may be avoided (Fig. 4). However, this advantage of SLPC has been overlooked for several years.

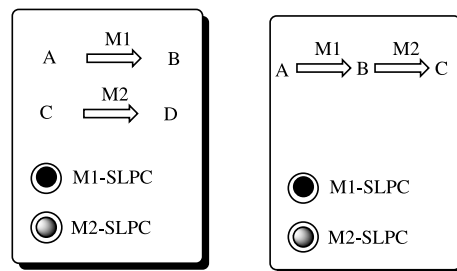
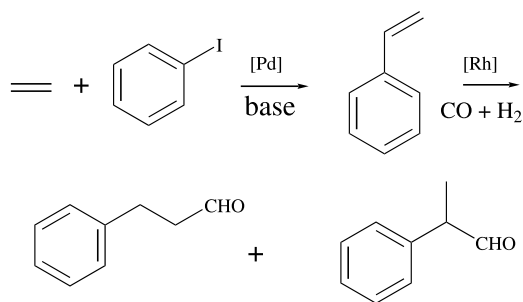


Fig. 4. Multifunctional multiphase catalytic systems using different SLPC samples at the same time, which are effective for one-pot parallel or sequential reactions.

Recently, we have reported such a multifunctional catalyst system using SLPC for sequential reactions involving Heck reaction followed by hydroformylation. (Scheme 2) [24]. It was shown that a physical mixture of Pd–SLPC and Rh–SLPC prepared individually is effective for these sequential reactions. However, when both Pd–TPPTS and Rh–TPPTS complexes are present in the same supported liquid film, the yield of the aldehyde is lowered, because the Rh–TPPTS complex is deactivated by the presence of the Pd–TPPTS complex in the same liquid film. It was also revealed that a mixture of Pd–SLPC and Ru–SLPC is effective for simultaneous hydrogenation of an olefin and aldehyde mixture. These results clearly demonstrate that effective application of two homogeneous catalysts retaining their individual activities is possible by using the SLPC technique. The concept of multifunctional catalyst system using different SLPC has broad ranging applications, since it allows using two or more metal complexes in the SLPC form in any combination of them. Additionally, SLPC is flexible in adjusting individual metal to ligand ratio and/or one metal to other metal combination ratio. Such cocktails of several metal complexes in the form of SLPC may also give new chemical transformations and contribute to the reduction of reaction steps (reactors).



Scheme 2. Sequential reactions of Heck coupling followed by hydroformylation, which are possible by using Pd–SLPC and Rh–SLPC in the same reactor (one-pot synthesis), as illustrated in Fig. 4.

6. Heck reaction using conventional Pd/C catalysts

In view of the practical and industrial applications, the use of heterogeneous catalysts may be promising. We have recently reviewed various attempts to use heterogeneous catalysis for Heck reaction [2]. Recently, we reported an interesting result of active metal dissolution and precipitation with a conventional carbon supported palladium catalyst for the Heck reaction of iodobenzene with methyl acrylate in *N*-methylpyrrolidone (NMP) in the presence of triethylamine and/or sodium carbonate (Fig. 5) [25–28]. At the initial stage of the reaction, active palladium complexes with the NMP and/or triethylamine molecules are formed in the solvent of NMP. Triethylamine is also considered to act as a reducing reagent of palladium. The palladium complex reacts easily with iodobenzene to start the catalytic cycle; the reaction proceeds homogeneously and the initial supported catalyst is a supplier and reservoir for the metal. After the completion of the reaction, the palladium complex re-deposits onto the support, since it is not stable in the absence of iodobenzene. Thus, the metal is recyclable without loss of any activity and selectivity performance. The use of both inorganic and organic bases is very effective in the promotion of palladium re-deposition as well as in the enhancement of the reaction rate. It is also found that, for Heck reaction of bromobenzene or chlorobenzene, the use of both triethylamine and sodium carbonate increases the selectivity of Heck coupling product (unfortunately, benzene is also produced in these cases as a byproduct), but the mixed bases do not affect the overall reaction rate.

7. Use of supercritical carbon dioxide as solvent for Heck reactions

Supercritical carbon dioxide (scCO₂) is gaining considerable interest as an ecologically benign and economically feasible new generation reaction medium, which can replace conventional toxic, flammable organic sol-

vents [29]. It allows various chemical substances to dissolve in it but it simply separates from them by depressurization, and its several other advantages are non-flammability, non-toxicity and absence of a gas–liquid phase boundary. The physicochemical properties of scCO₂ can be tuned within a certain range by adjusting the pressure and temperature. This will give us additional parameters for optimization of reactions [30]. Use of organometallic catalysts in scCO₂ is interesting, as described in the following sections.

7.1. Homogeneous catalysis in scCO₂

Although homogeneous organometallic catalysis in scCO₂ is attractive, the organometallic complexes should be dissolved in scCO₂. Often used phosphine ligands such as TPP are less soluble in scCO₂. However, the fluorination of the ligands improves their solubility [31] and hence metal complexes including fluorinated ligands can be effectively used in scCO₂. The solubility of metal complexes is a factor in determining the overall reaction rate, but the rate also depends on their specific activity. So, we have investigated a Pd-catalyzed Heck reaction of iodobenzene and styrene in scCO₂ using various fluorinated phosphine compounds as ligands (Scheme 3) under such conditions that all of the reacting species used can be dissolved in scCO₂ [32]. It has been found that the activity of palladium complexes strongly depends on the kind of phosphine compound used. The product yield obtained at CO₂ pressure of 12 MPa was in the order of **III** > **I** > **IV**, **II**, **V** > **VI**, **VII**, while that obtained at 8 MPa was **VI** > **I** > **IV** > **III** > **II** > **VII**. Although the solubility of fluorinated ligands is very high in dense CO₂, they have marginal improvements in Heck conversion in this medium compared with a non-fluorinated ligand of **I** (TPP). Visual observations and infrared spectroscopic measurements inside the reactor show that the reaction mixture is a single phase at 12 MPa, but biphasic at 8 MPa and the reaction proceeds in two phases, CO₂-rich phase and CO₂-poor liquid phase, at 8 MPa. These would result in the difference in

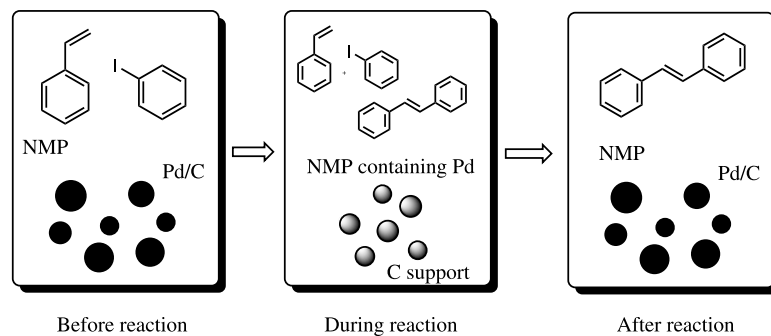
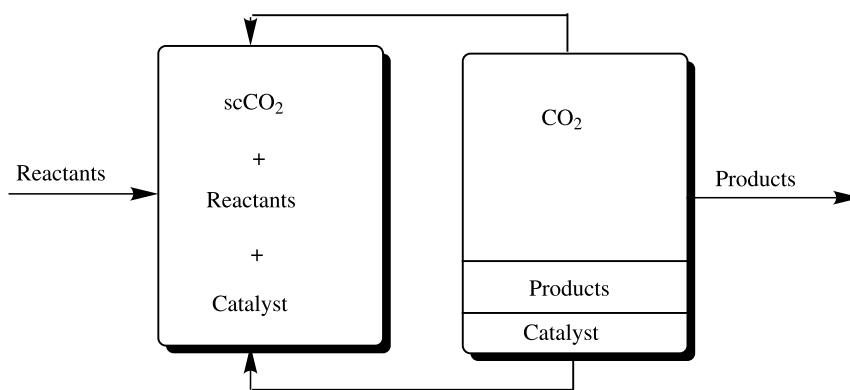
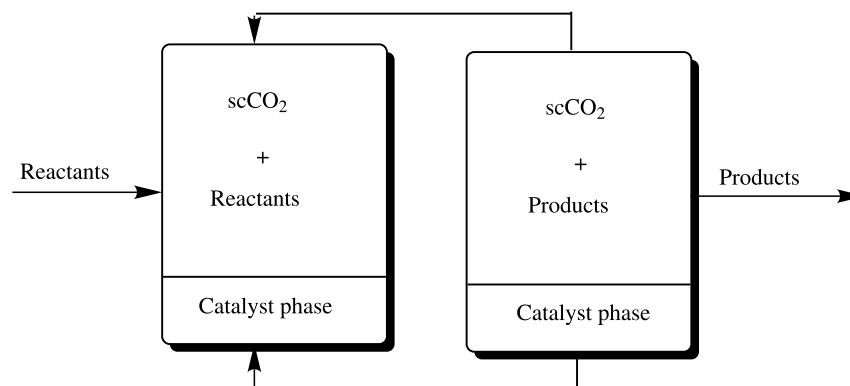


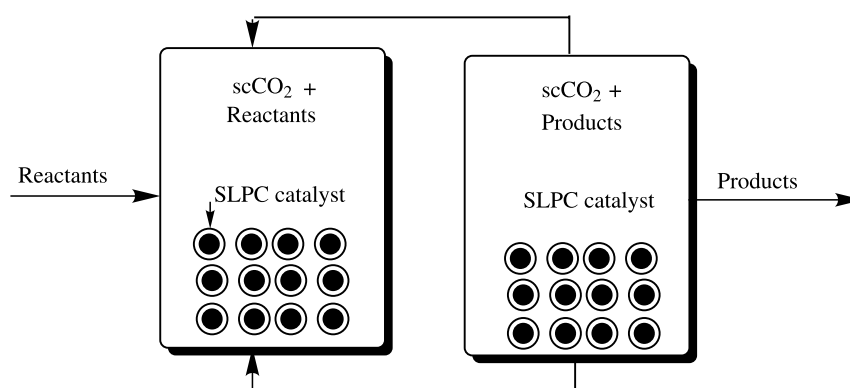
Fig. 5. Heck reaction using conventional Pd/C catalyst through transfer of the metal from and onto the C support. The reaction starts by dissolution of the metal, proceeds homogeneously by these active Pd species formed in the solvent, and ends followed by redeposition of the metal onto the support.



(A) Homogeneous/heterogeneous system using a cosolvent by which catalyst can be recovered.



(B) Biphasic system using a liquid phase (like water) that contains catalyst



(C) Two-phase system using SLPC

Fig. 6. Multiphase catalytic systems using supercritical carbon dioxide

7.3. Multiphase systems with catalyst product separation:

Similar to the above-mentioned scCO_2 -cosolvent system, the combination of scCO_2 and biphasic catalysis or SLPC gives benefit in the catalyst–product separation as shown in Fig. 6b and c. Unfortunately, we have not yet applied these systems for Heck reactions but they are effective for hydrogenation of α,β -unsaturated aldehyde with a Ru–TPPTS complex [36].

8. Concluding remarks

As demonstrated above for Heck reactions, the use of homogeneous Pd and other metal complexes catalysts in the different types of multiphase systems can bring several benefits such as easy catalyst product separation, catalyst recycling, and replacement for conventional organic solvents. For practical purposes, these may be more significant than high reaction rates with homogeneous systems.

It is also important to note that much effort has currently been made towards achieving good results with less reactive substrates, chlorides and bromides, using various homogeneous and heterogeneous systems. A few examples are: Studer et al. have reported the effectiveness of secondary phosphines as supporting ligands for Pd catalysts [37]. Sasson et al. reported the enhancement of the reactivity of chloroarenes by using a reducing agent, a mild base, and a phase-transfer catalyst in water [38]. Beller et al. have used monocarbenepalladium(0) complexes in an ionic liquid of Bu_4NBr [39]. Recent achievements are summarized in a review article [40].

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