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Carbon dioxide pressure induced heterogeneous and homogeneous Heck and Sonogashira coupling reactions using fluorinated palladium complex catalysts

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ABSTRACT

The Heck reaction of iodobenzene and methyl acrylate was investigated with CO_2-philic Pd complex catalysts having fluorous ponytails and the organic base triethylamine (Et_3N) in the presence of CO_2 under solventless conditions at 80°C. The catalysts are not soluble in the organic phase in the absence of CO_2 and the reaction occurs in a solid-liquid biphasic system. When the organic liquid mixture is pressurized by CO_2, CO_2 is dissolved into the organic phase and this promotes the dissolution of the Pd complex catalysts. As a result, the Heck reaction occurs homogeneously in the organic phase, which enhances the rate of reaction. This positive effect of CO_2 pressurization competes with the negative effect that the reacting species are diluted by an increasing amount of CO_2 molecules dissolved. Thus, the maximum conversion appears at a CO_2 pressure of around 4 MPa under the present reaction conditions. The catalysts are separated in the solid granules by depressurization and are recyclable without loss of activity after washing with *n*-hexane and/or water. When the washing is made with hexane alone, the catalytic activity tends to increase on the repeated Heck reactions, probably due to the accumulation of such a base adduct as Et_3NHI on the catalysts. When the washing is further made with water, however, the base adduct is taken off from the catalysts and they show similar activity levels in the repeated runs. The potential of CO_2 pressure tunable heterogeneous/homogeneous reaction system has also been investigated for Sonogashira reactions of iodobenzene and phenylacetylene under similar conditions.

Keywords: Carbon dioxide; Heck reaction; Sonogashira reaction; Multiphase reaction; Pressure effect; Fluorinated ligands; Catalyst recycling

1. Introduction

Homogeneous catalysis is superior to heterogeneous catalysis, making possible highly active and selective organic transformations. However, the separation and recovery of homogeneous catalysts are not easy and so it is still significant to prepare more active heterogeneous catalysts and to find effective ways of heterogenizing homogeneous catalysts for industrial reaction processes [1-3]. The phase behavior manipulation is an interesting tool for designing effective catalytic reaction and catalyst - product separation processes. Temperature is one of the parameters that can manipulate the phase behavior; for example, a solid catalyst is not soluble in an organic reaction mixture at ambient temperature but its solubility increases dramatically on heating, allowing the homogeneous catalysis to occur at elevated temperatures. On cooling after the reaction, the catalyst becomes separated and recovered in the solid phase and can be recycled. The advantages of these temperature-dependent thermomorphic reaction systems were demonstrated in previous works [4-7]. The Pd complexes having fluorous ponytailed bpy in the structure as shown in Scheme 1 were prepared and were successfully applied for thermomorphic Heck and Sonogashira reactions [8-11]. Those fluorous-ponytailed Pd complex catalysts are insoluble in polar organic solvents at room temperature but become soluble at > 120°C. Their thermomorphic mode of catalysis is possible without using any fluorous solvent but needs a relatively high temperature for total dissolution of the catalysts in the organic solvent phase.

Scheme 1

In the present work, the authors have applied CO_2-philic Pd catalysts shown in Scheme 1 for a liquid phase reaction of Heck coupling in the presence of CO_2 and investigated the potential of a CO_2 pressure tunable heterogeneous and homogeneous reaction medium for effective catalysis and catalyst separation/recycling. A simple Heck reaction [12-15] of iodobenzene and methyl acrylate has been selected as a test reaction. Recently it was indicated that the pressurization with CO_2 accelerated the rate of Heck reactions with a Pd-TPP (TPP: triphenylphosphine) complex catalyst for a few selected substrates although the reactions took place in homogeneous liquid phases and CO_2 was not a reactant [16]. One of important factors for this rate acceleration should be the presence of interactions of some groups of substrates and CO_2 molecules dissolved in the organic phase (toluene) under pressurized conditions [16-19]. That is, CO_2 can function as a reaction promoter for liquid-phase reactions as well as gas-liquid reactions such as oxidation [20-23], hydrogenation [24-30], and hydroformylation [31-33]. For the substrates of iodobenzene and methyl acrylate, however, no positive effect of CO_2 pressurization on the rate of Heck reaction was observed [16]. Thus, the Heck reaction of these substrates has been chosen in the present work because no gaseous reactants are included and interactions may be unlikely to occur between CO_2 molecules and the substrates. These features

are convenient for us to examine CO_2 pressure as a parameter for tuning the phase behavior. The present work will show that the CO_2 pressure can increase the solubility of the fluorinated catalysts in the neat organic substrate phase, promoting the rate of Heck reaction and the depressurization can cause the catalysts to precipitate from the liquid mixture, allowing them to be recycled. That is, the transformable heterogeneous and homogeneous catalysis can be achieved with the fluorinated catalysts and CO_2 without using additional organic and fluorous solvents, which are both needed for fluorous biphasic catalytic reactions [34-36]. The potential of the present CO_2 pressure tunable heterogeneous/homogeneous catalytic reaction system has also been studied for Sonogashira reaction [11, 37, 38] of iodobenzene and phenylacetylene under similar conditions. It is important to note here that our catalytic reaction systems are free of phosphine ligands, fluorinated solvents, and, possibly, conventional organic solvents. Previous workers studied carbon - carbon bond formation reactions in supercritical CO_2 using palladium complex catalysts with fluorinated ligands such as $(C_6F_{13}CH_2CH_2)_nPPh_{(3-n)}$ [39, 40] but the effects of CO_2 pressure tuning the catalyst activity, separation, and recycling were little mentioned.

The use of CO_2 as a miscibility switch was previously reported in several works of the groups of Eckert et al. and Jessop et al. using fluorous solvents and fluorinated metal complex catalysts [41-44]. These authors used bulk fluorous solvents and fluorous thin layers on the surface of a silica support; CO_2 pressure allows a catalyst-containing fluorous phase and a substrate-containing organic phase to merge into a single bulk liquid reaction phase. The CO_2 pressure changes the partition of a fluorinated catalyst between a bulk organic phase and the silica-supported fluorous layer, in which the catalyst partitions into the organic reaction phase under pressurized CO_2 conditions. The features of those CO_2-pressure tunable multiphase systems are demonstrated for reactions such as hydrogenation and epoxidation in the presence of gaseous reactants, as reviewed in a feature article [41]. The multiphase reaction media tunable by CO_2 pressure as well as temperature are expected to have practical merits and are still worth investigating for the process design of effective homogeneous catalysis and catalyst separation and recycling.

The phase behavior tunable multiphase catalytic reaction systems may be achieved by using other variables than CO_2 pressure and temperature, which include pH [45], magnetic field [46], and so on [45-48].

2. Experimental

2.1. Catalyst preparation

Gas chromatographic/mass spectrometric data were obtained using an Agilent 6890

series gas chromatograph with a series 5973 mass selective detector. The GC monitoring employed a HP 6890 GC using a 30 m x 0.250 mm HP-1 capillary column with a 0.25 μm stationary phase film thickness. Infrared spectra were obtained on a Perkin Elmer RX I FT-IR Spectrometer. NMR spectra were recorded on Bruker AM 500 and JEOL AM 200 using 5 mm sample tubes. CD_3OD, CD_2Cl_2, $CDCl_3$, deuterated DMF, and deuterated Me_2SO were used as references for both 1H and 13C NMR spectra; $CFCl_3$ was internal reference for 19F NMR spectra.

*2.1.1. Preparation of ligand, [4,4'-bis($R_f CH_2 OCH_2$)-2,2'-bpy] where $R_f = n\text{-}C_9F_{19}$ (**bpy-F19**) and $n\text{-}C_{11}F_{23}$ (**bpy-F23**)*

The $R_f CH_2 OH$ (6.0 mmol) and 30% $CH_3 ONa/CH_3 OH$ (1.1 g) were charged into a round-bottomed flask, then continuously stirred at 65 °C under N_2 atmosphere for 4 h before CH_3OH was vacuum removed to drive the reaction to the fluorinated alkoxide side. The resultant fluorinated alkoxide (6.0 mmol) was then dissolved in 20 mL of dry CH_3CN (or HFE 7100), and 4,4'-bis($BrCH_2$)-2,2'-bpy (5.8 mmol) added. The mixture was brought to reflux for 4 h, and the completeness of the reaction was checked by sampling the reaction mixtures and analyzing the aliquots with GC/MS. The product was purified by vacuum sublimation to obtain white solids.

Analytical data of **bpy-F19**: yield 72.4%; ^{1}H NMR (500 MHz, D-toluene, ppm) δ 8.53 (s, H_3, 2H), 8.51 (d, H_6, $^3J_{HH}$= 4.7 Hz, 2H), 6.93 (d, H_5, $^3J_{HH}$= 4.7 Hz, 2H), 4.18 (4H, s, bpy-C$\underline{H}_2$), 3.56 (4H, t, $^3J_{HF}$ = 13.3 Hz, $CF_2 C\underline{H}_2$); ^{19}F NMR (470.5 MHz, D-toluene) δ -81.0 (3F), -118.7 (t, -$CH_2 C\underline{F}_2$, $^3J_{HF}$= 12.9Hz, 2F), -121.1, -121.3, -122.1, -122.7, -125.6, (-$CH_2 CF_2 (C\underline{F}_2)_7 CF_3$, 14F); ^{13}C NMR (126 MHz, D-toluene) δ 73.5 (bpy-$\underline{C}H_2$), 68.2 ($\underline{C}H_2 CF_2$), 119.7, 121.9, 146.9, 149.9, 157.2 (bpy), 105.0~116.0 ($\underline{C}_{10}F_{21}$); GC/MS (m/z; EI): 682 (M^+-$OCHC_9F_{19}$), 183 ($C_5H_3NCH_2C_5H_3NCH_3^+$), 91 ($C_5H_3NCH_2^+$); FT-IR (cm^{-1}): 1599, 1463 ($v$bpy, m), 1208, 1144 ($v CF_2$, vs); m.p.: 125-128°C.

Analytical data of **bpy-F23**: : yield 63.2%; ^{1}H NMR (500 MHz, D-toluene, ppm) δ 8.52 (s, H_3, 2H), 8.51 (d, H_6, $^3J_{HH}$= 4.7 Hz, 2H), 6.93 (d, H_5, $^3J_{HH}$= 4.7 Hz, 2H), 4.19 (4H, s, bpy-C$\underline{H}_2$), 3.59 (4H, t, $^3J_{HF}$ = 13.3 Hz, $CF_2 C\underline{H}_2$); ^{19}F NMR (470.5 MHz, D-toluene) δ -81.1 (t, -CF_3, $^3J_{FF}$= 9.67Hz, 3F), -118.7 (t, -$CH_2 C\underline{F}_2$, $^3J_{HF}$= 12.9 Hz, 2F), -121.1, -121.3, -122.2, -122.7, -125.7 (-$CH_2 CF_2 (C\underline{F}_2)_9 CF_3$, 18F); ^{13}C NMR (126 MHz, D-toluene) δ 73.5 (bpy-$\underline{C}H_2$), 68.2 ($\underline{C}H_2 CF_2$), 119.6, 122.8, 146.9, 149.9, 157.2 (bpy), 105.0~116.0 ($\underline{C}_{10}F_{21}$); GC/MS (m/z; EI): 782 (M^+-$OCHC_{11}F_{23}$), 183 ($C_5H_3NCH_2C_5H_3NCH_3^+$), 91 ($C_5H_3NCH_2^+$); FT-IR (cm^{-1}): 1599, 1463 ($v$bpy, m), 1208, 1150 ($v CF_2$, vs); m.p.: 147-150°C.

Compared to another fluorous bpy ($CF_3(CF_2)_5(CH_2)_3$-$C_5H_3N)_2$ with m.p. 113-115°C

[49], the bpy-F19 and bpy-F23 prepared showed higher melting points by about 13 K and 35 K, respectively.

2.1.2. Preparation of Pd-F19 and Pd-F23

Equimolar amounts of [PdCl$_2$(CH$_3$CN)$_2$] (134.9 mg, 0.52 mmol) and respective ligands, bpy-F19 and bpy-F23, (0.52 mmol) in different reactions were charged into a round bottomed flask, and CH$_2$Cl$_2$ (3 mL) added as solvent. The solution color changed from red to yellow after the mixing for several min. The solution was further stirred at 60 °C for 24 h before the solvents and volatiles were removed under vacuum. The resulting yellow solids were collected as spectroscopically pure products.

Analytical data of **Pd-F19** (NMR data collected in d-DMF at 90 °C because of poor solubility): yield 96%; ^{1}H NMR (500 MHz, DMF-d_6, δ ppm, J Hz) 9.29 (d, 2H, $^3J_{HH}$= 5.8, H_6), 8.47 (s, 2H, H_3), 7.81 (d, 2H, $^3J_{HH}$= 5.8, H_5), 5.08 (s, 4H, bpy-CH_2), 4.47 (t, 4H, $^3J_{HF}$= 14.6, C$_{10}$F$_{21}$-CH_2); ^{19}F NMR (470.5 MHz, DMF-d_6, δ ppm, J Hz) -80.9 (t, 6F, $^3J_{FF}$= 7.52, -CF_3), -119.3 (4F), -121.2 (16F), -122.2 (4F), -122.8 (4F), -125.6 (4F); ^{13}C NMR (126 MHz, DMF-d_7, δ ppm) 72.4 (bpy-CH$_2$), 68.2 (CH$_2$CF$_2$), 121.5, 125.0, 150.5, 153.0, 157.0 (bpy), 105.0~116.0 (C_{10}F$_{21}$); FT-IR (KBr pellets, v_{max}/cm^{-1}): 1624, 1561 (m, vbpy) 1207, 1148 (vs, vCF$_2$); HR-MS (FAB) (JEOL JMS-700): (M$^+$; m/z=) C$_{32}$N$_2$H$_{14}$F$_{38}$O$_2$Pd^{35}Cl$_2$ calcd 1355.8860, found 1355.8823; C$_{32}$N$_2$H$_{14}$F$_{38}$O$_2$Pd^{37}Cl^{35}Cl calcd 1357.8864, found 1357.8848; C$_{32}$N$_2$H$_{14}$F$_{38}$O$_2$Pd^{37}Cl$_2$ calcd 1359.8835, found 1359.8792.

Analytical data of **Pd-F23** (NMR data collected in d-DMF at 90 °C because of very poor solubility): yield 90.4 %; ^{1}H NMR (500 MHz, DMF-d_7, δ ppm, J Hz) 9.29 (d, 2H, $^3J_{HH}$= 5.8, H_6), 8.47 (s, 2H, H_3), 7.81 (d, 2H, $^3J_{HH}$= 6.0, H_5), 5.09 (4H, s, bpy-CH_2), 4.48 (t, 4H, $^3J_{HF}$= 14.29, C$_{10}$F$_{23}$-CH_2); ^{19}F NMR (470.5 MHz, DMF-d_7, δ ppm, J Hz) -81.0 (t, 6F, $^3J_{FF}$= 7.5, -CF_3), -119.3 (4F), -121.3 (24F), -122.2 (4F), -122.9 (4F), -125.7 (4F); ^{13}C NMR (126 MHz, DMF-d_7, δ ppm): ^{13}C NMR spectrum was not obtained due to the extremely weak signal at 90 °C; FT-IR (KBr pellets, v_{max}/cm^{-1}): 1602, 1558 (m, vbpy), 1207, 1152 (vs, vCF$_2$); HR-MS (FAB): (M$^+$; m/z=) C$_{36}$N$_2$H$_{14}$F$_{46}$O$_2$Pd^{35}Cl$_2$ calcd 1555.8732, found 1555.8721; C$_{36}$N$_2$H$_{14}$F$_{46}$O$_2$Pd^{37}Cl^{35}Cl calcd 1557.8679, found 1557.8656; C$_{36}$N$_2$H$_{14}$F$_{46}$O$_2$Pd^{37}Cl$_2$ calcd 1559.8674, found 1559.8662.

2.2. Heck and Sonogashira reactions

A stainless steel autoclave reactor (50 cm^3) was used to run Heck reactions without any organic solvent pressurized with CO$_2$ at different pressures up to 16 MPa. Typical reaction conditions were: catalyst (Pd-F19, Pd-F23) 0.025 mmol (1 mol% to iodobenzene), iodobenzene 2.5 mmol, methyl acrylate 3.75 mmol, triethylamine 3.75 mmol. All the chemicals (Wako or

Aldrich) were used as received. The reactor was charged with these quantities of substrates, base, and catalyst and purged with CO_2 three times. The reactor was then heated in an oil bath while mixing the reaction mixture by a Teflon-coated magnetic stirrer. When the reactor temperature reached the desired value of $80\,^{\circ}C$, CO_2 was introduced to the desired pressure by a backpressure regulator (JASCO SCF-Bpg) and the reaction time was measured. After the reaction for 4 h, the reactor was cooled down to room temperature and depressurized carefully. The reaction products were analyzed by gas chromatograph (GL Science GC-390B, TC1701 capillary column) using anisole as internal standard and gas chromatograph - mass spectrometer (Shimadzu GC-MS QP5050A). The conversions were determined from the amounts of iodobenzene reacted. For Sonogashira reaction of iodobenzene and phenylacetylene, the same reactor and similar reaction and analysis procedures were also used. Sonogashira reactions were run at 80°C for 4 h under the following conditions: iodobenzene 2.5 mmol, phenylacetylene (Wako) 3.75 mmol, and triethylamine 3.75 mmol.

2.3. Phase behavior measurements

The phase behavior was examined by visual observation using an autoclave with a transparent glass window. A desired volume of liquid phase was added to the autoclave with a volume ratio of liquid/autoclave to be similar to that used in Heck reaction runs. An atmospheric pressure of CO_2 was introduced and the autoclave was closed and heated to the desired reaction temperature of 80°C. While keeping the autoclave at this temperature, more CO_2 was introduced into the autoclave up to higher pressures. The phase behavior was visually examined at different CO_2 pressures.

The relative amounts of Pd-F19 and Pd-F23 catalysts dissolved in CO_2 gas phase were measured at a reaction temperature of 80°C as a function of CO_2 pressure by in situ high pressure FTIR measurements using the same apparatus and procedures as described previously [18]. The results are helpful for considering the affinity between the catalysts and CO_2 molecules in not only the CO_2 gas phase but also a liquid phase dissolving a large quantity of CO_2 under high pressure conditions.

For Sonogashira reactions, the amount of Pd species present in the organic liquid phase was measured after the reaction runs with inductively coupled plasma optical emission spectrometry (Thermo, ICP-OESCICAP 6300).

3. Results and discussion

3.1. Heck reactions under pressurized CO$_2$ conditions

As the main theme of this work, the authors applied fluorinated Pd complex catalysts Pd-F19 and Pd-F23 (Scheme 1) for the Heck reaction under pressurized CO_2 conditions. Heck reactions of iodobenzene and methylacrylate were conducted with triethylamine as a base under solventless conditions in the presence of CO_2 (system (a) in Fig. 1). For comparison the same Heck reactions were also carried out using a fluorous solvent, perfluorooctane (system (b)). In these reactions, the selectivity of Heck coupling was 100% under the conditions used. The Heck reactions using an organic solvent, toluene, and a Pd-TPP complex catalyst under pressurized CO_2 conditions (system (c)) were already studied in a previous work [16]. These multiphase Heck reaction systems at ambient CO_2 pressure are illustrated in Fig. 1 and the results obtained in these systems at increasing CO_2 pressures will be compared in Fig.2. Both Pd-F19 and Pd-F23 complexes are not soluble in the organic reaction mixture of system (a) under ambient conditions, but soluble in perfluorooctane of system (b). In system (c), the Pd-TPP complex without fluorous ponytail is soluble in toluene but it is less CO_2-philic and so it is little soluble in CO_2. When the toluene phase is pressurized by CO_2 at elevated pressures, a large amount of CO_2 exists in this phase and this would decrease the amount of the Pd-TPP complex dissolved. In addition, the Pd-TPP becomes soluble in the organic phase on depressurization after the reaction, so its separation and recycling are not easy. In contrast, Pd-F19 and Pd-F23 complexes are insoluble in a neat organic liquid but they become soluble when the organic liquid is pressurized by CO_2. The phase behavior of the fluorinated Pd-F19 and Pd-F23 complexes in the liquid - CO_2 system is opposite to that of the non-fluorinated Pd-TPP complex.

Figure 1

The results obtained with system (a) at different CO_2 pressures are shown in Fig. 2 (1). It is interesting to note that the conversion increases with the pressure and it takes a maximum at around 4 MPa in similar manners for the two fluorinated Pd complex catalysts, Pd-F19 and Pd-F23. The maximum conversion levels obtained with Pd-F19 and Pd-F23 are larger by factors of 2.3 and 1.6, respectively, compared with those in the absence of CO_2. Fig. 2 (2) gives the results with system (b) using one of the fluorinated Pd complexes, Pd-F23. The conversion level measured under ambient CO_2 atmosphere is similar to the previous one obtained in system (a); in contrast, however, the conversion merely decreases with CO_2 pressure. It was previously reported that the pressurization of system (c) with CO_2 only caused a decrease in the conversion for the same substrates, similar to the present results with system (b) [16]. Such a decrease in the conversion may be ascribable to a simple dilution of the reaction phases (organic and/or fluorous) by dissolution of a large quantity of CO_2 molecules at high pressures.

Figure 2

3.2. Phase behavior under pressurized CO$_2$ conditions

The pressure at which the reaction mixture changed into a single phase was examined at different temperatures using the same relative volumes of organic compounds (iodobenzene, methyl acrylate, triethylamine) with respect to the reactor volume as used in the Heck reaction runs. Fig. 3 gives the results of this phase behavior observation, indicating that a higher CO$_2$ pressure is needed for the liquid-gas mixture to change into a single gas phase as the temperature is raised. At a reaction temperature of 80°C, the phase change occurs at a CO$_2$ pressure > 11 MPa.

Figure 3

Further, the phase behavior of reaction mixture was examined at 80°C and at different CO$_2$ pressure. In this examination, the initial volume ratio of liquid phase to reactor under ambient conditions was very similar to that used in the above-mentioned Heck reaction runs. It was found, for the system (a) of Fig. 1, that when the mixture of organic compounds (iodobenzene, methyl acrylate, triethylamine) was pressurized by CO$_2$, the liquid phase expanded but very slightly at pressures up to 7 MPa, its volume became decreased at 8 - 10 MPa, and then the gas - liquid mixture changed into a single phase at 11 MPa. As mentioned above, the maximum Heck conversion appears at a lower pressure of about 4 MPa (Fig. 2(1)); namely, the conversion can be maximal under gas-liquid biphasic conditions. Similar volume change was observed for perfluorooctane in the absence of organic compounds, but a single phase state appeared at a lower pressure of 8.4 MPa. (Note: For the system (a), the volume of the organic species was small, so it was difficult to see the liquid-gas boundary). Fig. 4 shows the phase behavior of system (b) - i.e. the change of the state of mixture of iodobenzene, methyl acrylate, triethylamine, and perfluorooctane with CO$_2$ pressure. The liquid phase expanded slightly at pressures up to 7 MPa and it merged into a single phase at > 11 MPa. For this reaction mixture in which the catalyst was dissolved in the fluorous phase, the Heck conversion decreased monotonously with CO$_2$ pressure (Fig. 2(2)).

Figure 4

The affinity of Pd-F19 and Pd-F23 with CO$_2$ molecules was examined by high pressure FTIR measurements at a reaction temperature of 80°C. Similar FTIR spectra were obtained for these catalysts. Fig. 5 gives selected FTIR spectra for Pd-F23 catalyst dissolved in CO$_2$ gas phase at different pressures. Two absorption bands can be seen at 1149 cm^{-1} and 1203 cm^{-1}, which are assigned to stretching vibrations of CF$_2$ [50]. The peaks of these absorption bands in pressurized CO$_2$ are slightly red-shifted as compared with those located at 1152 cm^{-1} and 1207 cm^{-1} for the solid sample (diluted with KBr) under ambient conditions. The absorption peak

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positions were often found to be shifted by the presence of CO_2 [18]. The absorbance at 1149 cm^{-1} was herein used to estimate the relative amounts of the two fluorinated catalysts dissolved in CO_2 as a function of pressure (Fig. 6). The two catalysts are little soluble in atmospheric CO_2 but they can be soluble at a pressure of 4 MPa. The strength of the absorption band little changes at higher CO_2 pressures for the two catalysts. The strength of absorption band of an organic sample dissolved in CO_2 gas phase does not always increase monotonously with the CO_2 pressure although it is believed to be more soluble at higher pressures [18]. From the present FTIR results, it can be said that the catalysts are CO_2-philic and should become more soluble in CO_2 gas phase with increase in the CO_2 pressure. It is assumed, therefore, that the dissolution of a large amount of CO_2 into an organic liquid phase will promote the dissolution of the catalysts in this liquid phase, which are changed to more CO_2-philic.

Figure 5, Figure 6

3.3. Impact of CO_2 pressurization

For the solventless Heck reaction with the fluorinated Pd catalysts, the conversion can be enhanced in the presence of CO_2 at pressures up to around 4 MPa (Fig. 2 (1)). The maximum conversion appears at very similar CO_2 pressures for the two catalysts. At these pressures < 4 MPa the organic liquid phase exists and so the reaction occurs in this phase. When the liquid phase is pressurized by CO_2, more CO_2 is dissolved in it, promoting the dissolution of the CO_2-philic Pd catalyst into the liquid phase. This is one of significant factors for the enhancement of Heck reaction on CO_2 pressurization. The affinity with CO_2 molecules is very similar between the two catalysts Pd-F19 and Pd-F23 at pressures examined < 25 MPa (Fig. 6) and this can explain that the maximum effects of CO_2 pressurization appear at similar pressures of around 4 MPa. The further pressurization (CO_2 dissolution) lowers the concentration of reacting species in the liquid phase. This dilution effect causes the decrease in the Heck conversion at higher CO_2 pressures. One can consider other possible factors responsible for the rate enhancement on pressurization with CO_2. One is interactions of CO_2 dissolved in the liquid phase with some reacting species, substrates and/or catalyst, which are previously assumed to be a significant factor responsible for the similar rate acceleration in Heck reactions with a non-fluorinated Pd/TPP catalyst [16]. Another factor is a change of mass transfer rate, which may be improved in the CO_2 dissolved liquid phase as compared with the non-pressurized phase. However, this factor should not be important because the effects of CO_2 pressure are different for several substrates that are similar in the molecular weight (similar diffusivity) under the reaction conditions used [16]. Future work is required to study the reaction mechanisms and kinetics for reactions in the CO_2 dissolved liquid phase and the CO_2-rich single gas phase.

When perfluorooctane is also used, the reaction mixture consists of organic liquid and

CO_2 gas phases in addition to the fluorous phase dissolving the catalyst. The fluorinated Pd catalyst is present in the latter phase and the Heck reaction should occur at the organic - fluorous interface. The dissolution of CO_2 on pressurization is likely to dilute the reactants in the organic phase and the catalyst in the fluorous phase. This would cause only a decrease in the rate of Heck reaction, as observed (Fig. 2 (2)).

3.4. Catalyst recycling test in system (a)

The catalyst recycling is one of important aspects for practical application. Here the catalyst reusability was examined in system (a) using a catalyst of Pd-23F. Presumably, the conversion was proportional to the reaction time and catalyst amount. Thus, the catalyst reusability in the presence of CO_2 was conducted as follows: after a Heck reaction run, the catalyst (fine granules) was separated by decantation, washed with *n*-hexane twice, dried in the reactor under ambient conditions, and then used for the next run under the same reaction conditions. It is interesting to note that the catalytic activity tends to increase on the repeated runs (Fig. 7). This increase is the same as observed for the Heck reactions with a supported liquid phase catalyst of Pd-TPPTS in ethylene glycol film using the organic base Et_3N [51]. This was previously explained by the effect of base adduct, Et_3NHI, which should be related with the promotion effect of so-called Jeffery conditions [52]: palladium(II) salts were combined with tetrabutylammonium halide additives. In the present system (a) as well, the base adduct is formed during the reaction and it cannot be taken off from the catalyst (solid) by washing with a non-polar organic liquid, *n*-hexane. Thus, the base adduct should be accumulated on the catalyst and play a role for increasing the catalytic activity on the repeated runs. When the catalyst was also washed with distilled water following the washing with *n*-hexane, however, the catalyst was observed to show similar activities for several reaction runs, as seen in Fig. 7. It is assumed that the base adduct is removed by water and does not remain on the catalyst. Thus, the catalyst can be recycled with no appreciable change of activity in system (a).

Figure 7

3.5. Application to Sonogashira coupling

The potential of the above-mentioned CO_2 pressure tunable heterogeneous/ homogeneous reaction medium has also been examined for Sonogashira coupling of iodobenzene and phenylacetylene [11] under the same conditions as used for Heck reaction runs. Under the conditions used, in addition to the Sonogashira coupling product, a small amount of the homo coupling product 1, 4-diphenylbutadiyne was observed to form. Fig. 8 shows the results obtained with a catalyst, Pd-F19, at different CO_2 pressures. The conversion obtained under ambient conditions is 64%, which is larger than the one (17%) of Heck coupling. The

pressurization with CO_2 is also effective for enhancing the conversion but the extent of enhancement is less and the maximum conversion appears at a lower pressure of around 2 MPa compared with the results of Heck reactions (Fig. 2). The differences between these two coupling reactions may result at least in part from the difference in the chemical nature between phenylacetylene and methyl acrylate (the other reacting species are the same: iodobenzene, triethylamine, fluorinated Pd complex catalyst).

Figure 8

Although the catalyst separation and recycling is easy through a simple decantation for the Heck reaction as above-mentioned, centrifugal separation was required to separate the solid catalyst well from the liquid in the case of the Sonogashira reactions. Fig. 9 shows that the conversion decreases on the repeated runs, becoming decreased to half the first conversion for the third run (second recycling run). The changes were the same when either *n*-hexane or distilled water was used for the washing of solid material after centrifugal separation. For the case of Heck reactions, the base adduct was removed by washing with water but not hexane, and the conversion changed in different fashions depending on the presence and absence of the base adduct (Fig. 7). In addition, a marginal amount of 1, 4-diphenylbutadiyne was also formed in the third run. The authors speculate at present that the selection of base plays an important role in the Sonogashira reactions, and the use of organic base, Et_3N, instead of inorganic base might be one of important factors responsible for the decrease of activity on repeated runs [11]. In addition, the solubility of catalyst in the liquid phase might be another factor; phenylacetylene is present instead of methyl acrylate, and so the solvent properties may be different between Sonogashira and Heck reactions. The amounts of Pd present in the organic phase after the first and second (1st recycling) runs were 13% and 14%, respectively, of the initial amount of Pd used. Namely, some fraction of Pd catalyst was unable to precipitate and separate from the organic liquid phase although the centrifugal separation was made after the reactions. This is also another factor to explain the decrease in the activity on repeated Sonogashira reactions (Fig. 9). This incomplete recovery of the Pd catalyst might result from a change in its chemical nature caused by the organic base as mentioned above, which would change the catalyst from CO_2-philic to less CO_2-philic (oleophilic), causing it to finely disperse in the organic liquid phase and to become soluble in the liquid phase even after the CO_2 depressurization.

Figure 9

4. Conclusions

The present results demonstrate that the CO_2 pressure tunable homogeneous and

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heterogeneous catalytic system can be achieved for the Heck reaction of iodobenzene and methyl acrylate using CO_2-philic fluorinated Pd complex catalysts in the neat organic substrate and base liquid phase. That is, our catalytic reaction systems are free of phosphine ligands, fluorinated solvents, and conventional organic solvents. The CO_2 pressure is a variable changing the solubility of the catalysts in the liquid phase and the Heck reaction occurs in a homogeneous phase at CO_2 pressures > 4 MPa but in a liquid - solid (catalyst) heterogeneous mixture under ambient conditions. Under the reaction conditions used, the maximum effect of CO_2 pressurization appears at a pressure of around 4 MPa, above which the simple dilution of the reacting species by the dissolution of CO_2 molecules into the organic liquid phase is more significant, decreasing the rate of reaction. The catalysts are easy to separate on depressurization after reaction and can be recycled; when the catalysts are washed with *n*-hexane, they show increasing activity due to the accumulation of base adduct; when washed with water, however, they indicate very similar activities for repeated Heck reaction runs, due to the dissolution/removal of the base adduct by water. For Sonogashira reaction of iodobenzene and phenylacetylene without using any organic solvent, the CO_2 pressurization has a similar impact on the rate of reaction under the same concentration conditions as used for the Heck reactions but the maximum impact appears at a lower pressure of around 2 MPa. However, centrifugal separation is required to separate and recover the catalyst.

Acknowledgement

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Captions to Scheme 1 and Figures 1 - 9:

Scheme 1.   Fluorinated palladium complex catalysts, Pd-F19 and Pd-F23, used in this work (the word "fluorinated" is used to mean a molecule containing a large content of fluorine.)

Fig. 1.   Multiphase Heck reaction systems studied in this work (the phases existing under ambient conditions are shown). These reaction systems include iodobenzene, methylacrylate, and triethylamine. No additional solvent is used in system (a) while a fluorous liquid (perfluorooctane) and an organic liquid (toluene) in systems (b) and (c), respectively. Fluorinated Pd complex catalysts are used in systems (a) and (b) while Pd-TPP complex catalyst in system (c).

Fig. 2.   Results of Heck reactions in the absence of additional solvent (1) and in the presence of perfluorooctane (2) under CO_2 pressurized conditions. *Reaction conditions*: reactor volume 50 cm^3, iodobenzene 2.5 mmol, methyl acrylate 3.75 mmol, triethylamine 3.75 mmol, perfluorooctane 1.14 cm^3, catalyst 0.025 mmol (1mol% to iodobenzene), temperature 80°C, time 4 hours

Fig. 3.   Phase transition pressure against temperature for organic liquid mixture pressurized by CO_2. *Conditions*: reactor 10 cm^3, iodobenzene 0.5 mmol, methyl acrylate 0.75 mmol, triethylamine 0.75 mmol (total ca. 0.2 cm^3)

Fig. 4.   Results of the phase behavior observations for the liquid mixture of organic species (iodobenzene, methyl acrylate, triethylamine) and a fluorous liquid of perfluorooctane in the presence of dense phase CO_2 at 80°C and at different pressures given. The relative volumes of the organic and fluorous species against the reactor volume were the same as used in the hydrogenation runs. The line across the pictures indicates the initial liquid - gas interface at 0.1 MPa CO_2 pressure.

Fig. 5.   FTIR spectra of Pd-F23 catalyst dissolved in dense phase CO_2 at 80°C and at different CO_2 pressures given and in the solid state mixed with KBr under ambient conditions.
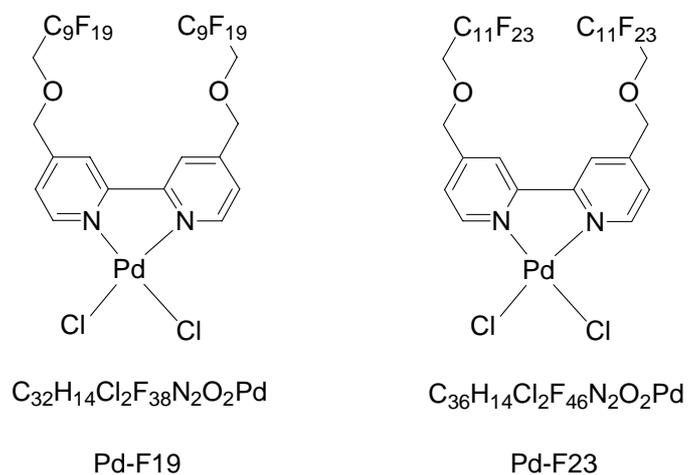
Fig. 6.   Changes of the absorbance at ~1150 cm^{-1} due to CF_2 stretching vibration with CO_2 pressure for Pd-F19 ( ) and Pd-F23 (○) catalysts dissolved in dense phase CO_2 at 80°C.

Fig. 7. Results of catalyst recycling test. *Reaction conditions*: iodobenzene 2.5 mmol (0.279 ml), methyl acrylate 3.75 mml (0.337 cm^3), triethylamine 3.75 mmol (0.552 cm^3); catalyst Pd-F23 20 mg, temperature 80°C, time 1 h, CO_2 4 MPa. After one reaction run, the liquid phase was removed by decantation and the remaining materials (solid catalyst with a very small volume of liquid) were washed by *n*-hexane (5 cm^3) twice (procedure A) and further by distilled water (5 cm^3) twice (procedure B), after which the catalyst was dried under ambient conditions and then used for next run with fresh substrates and base.

Fig. 8. Results of Sonogashira reactions in the presence of dense phase CO_2. *Reaction conditions*: reactor volume 50 cm^3, iodobenzene 2.5 mmol, phenylacetylene 3.75 mmol, triethylamine 3.75 mmol, catalyst Pd-F19 0.025 mmol (1mol% to iodobenzene), temperature 80 °C, time 4 hours.

Fig. 9. Results of catalyst recycling test. *Reaction conditions*: reactor volume 50 cm^3, iodobenzene 2.5 mmol, phenylacetylene 3.75 mmol, triethylamine 3.75 mmol, catalyst Pd-F19 0.025 mmol (1mol% to iodobenzene), temperature 80°C, time 4 hours. After a reaction run, the reaction mixture was subjected to centrifugal separation and decantation. The residual solid material was washed with toluene twice followed by washing with *n*-hexane (procedure A) or distilled water (procedure B) twice. Then the solid material was used for the next run.

Scheme 1 and Figures 1 - 7 in the order of appearance:

$C_{32}H_{14}Cl_2F_{38}N_2O_2Pd$

Pd-F19

$C_{36}H_{14}Cl_2F_{46}N_2O_2Pd$

Pd-F23

Scheme 1. Fluorinated palladium complex catalysts, Pd-F19 and Pd-F23, used in this work (the word "fluorinated" is used to mean a molecule containing a large content of fluorine.)
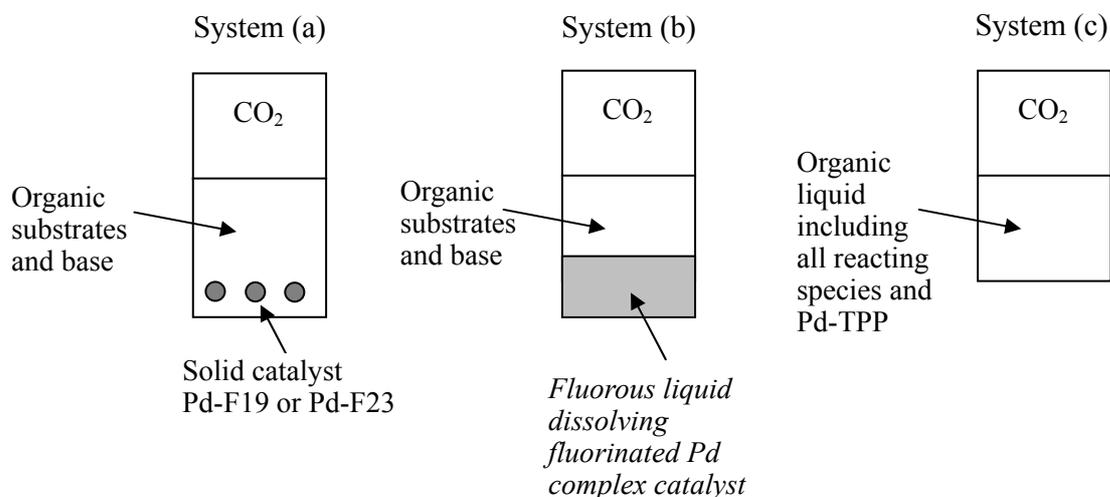
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Fig. 5.   FTIR spectra of Pd-F23 catalyst dissolved in dense phase CO_2 at 80°C and at different CO_2 pressures given and in the solid state mixed with KBr under ambient conditions
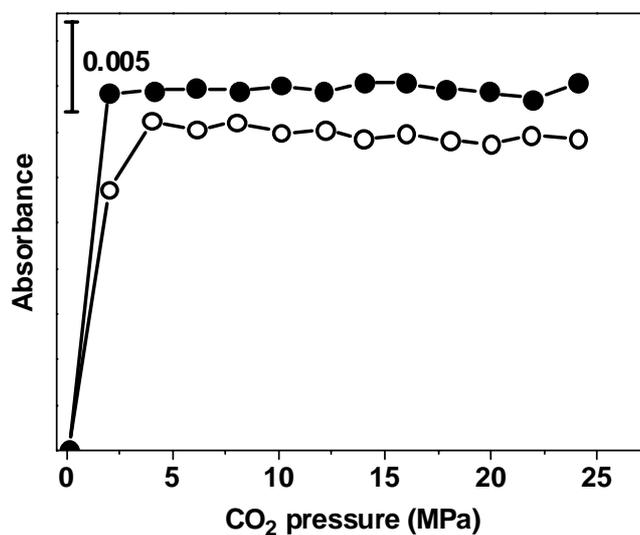

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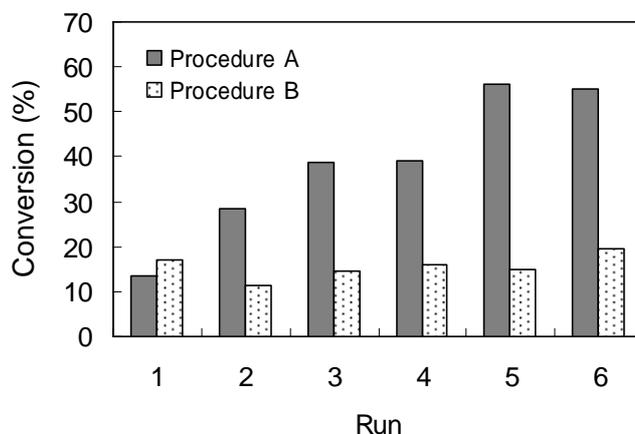
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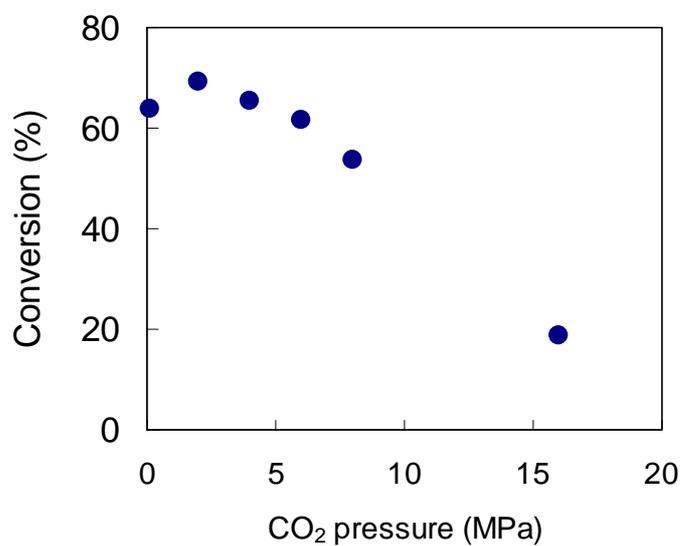
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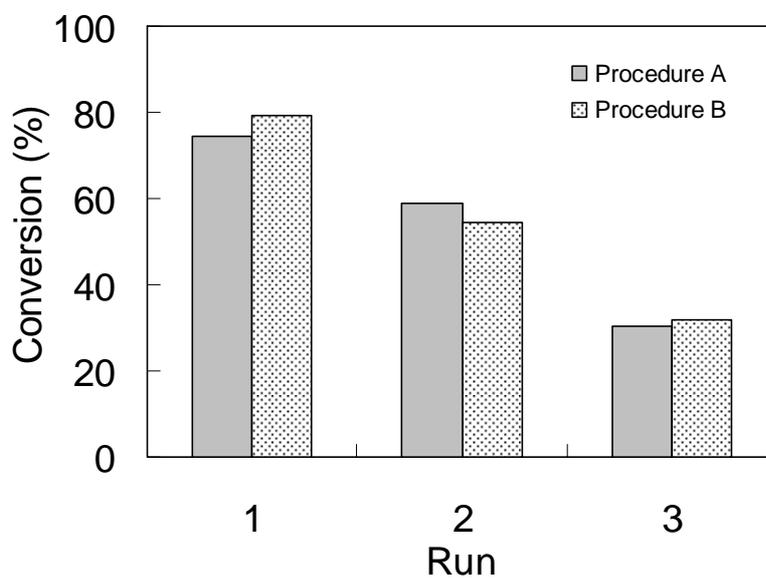
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