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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.

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.

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

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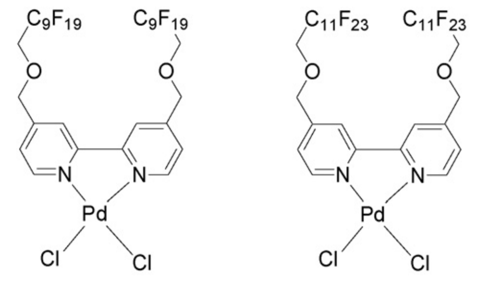

$C_{32}H_{14}Cl_2F_{38}N_2O_2Pd$ $C_{36}H_{14}Cl_2F_{46}N_2O_2Pd$

Pd-F19 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).

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 [11,13,37] 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 $(C_6F_{13}CH_2CH_2)_nPPh_{(3-n)}$ [38,39] 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 [40–43]. 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 [40]. 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 [44], magnetic field [45], and so on [44–47].

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 × 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($R_fCH_2OCH_2$)-2,2′-bpy] where R_f = n-C_9F_{19} (bpy-F19) and n-$C_{11}F_{23}$ (bpy-F23)

The R_fCH_2OH (6.0 mmol) and 30% CH_3ONa/CH_3OH (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, $CF_2C\underline{H}_2$); ^{19}F NMR (470.5 MHz, D-toluene) δ −81.0 (3F), −118.7 (t, $-CH_2C\underline{F}_2$, $^3J_{HF}$ = 12.9 Hz, 2F), −121.1, −121.3, −122.1, −122.7, −125.6 ($-CH_2CF_2(C\underline{F}_2)_7CF_3$, 14F); ^{13}C NMR (126 MHz, D-toluene) δ 73.5 (bpy-$\underline{C}H_2$), 68.2 ($\underline{C}H_2CF_2$), 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 ($C_5H_3NCH_2^+$); FTIR (cm^{-1}): 1599, 1463 (νbpy, m), 1208, 1144 (νCF_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, $CF_2C\underline{H}_2$); ^{19}F NMR (470.5 MHz, D-toluene) δ −81.1 (t, $-CF_3$, $^3J_{FF}$ = 9.67 Hz, 3F), −118.7 (t, $-CH_2C\underline{F}_2$, $^3J_{HF}$ = 12.9 Hz, 2F), −121.1, −121.3, −122.2, −122.7, −125.7 ($-CH_2CF_2(C\underline{F}_2)_9CF_3$, 18F); ^{13}C NMR (126 MHz, D-toluene) δ 73.5 (bpy-$\underline{C}H_2$), 68.2 ($\underline{C}H_2CF_2$), 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 ($C_5H_3NCH_2^+$); FTIR (cm^{-1}): 1599, 1463 (νbpy, m), 1208, 1150 (νCF_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 [48], the bpy-F19 and bpy-F23 prepared showed higher melting points by about 13 and 35 K, respectively.

2.1.2. Preparation of Pd-F19 and Pd-F23

Equimolar amounts of $[PdCl_2(CH_3CN)_2]$ (134.9 mg, 0.52 mmol) and respective ligands, bpy-F19 and bpy-F23 (0.52 mmol) in dif-