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Heck reactions using water-soluble metal complexes in supercritical carbon dioxide

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Abstract

Heck vinylation reaction was studied using $Pd(OAc)_2$/TPPTS catalyst system in supercritical carbon dioxide. The addition of co-solvents such as water and ethylene glycol significantly enhances the rate of reaction without leaching of Pd into the product phase. The reactants/products can be easily separated from the catalyst by simple phase separation and the catalyst can be recycled. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The increasing concern towards environmentally friendly and efficient processes in chemical manufacturing has led to a growing need for processes that produce minimal waste and avoid, as much as possible, the use of toxic and/or hazardous reagents and solvents. Supercritical carbon dioxide ($ScCO_2$) is considered as an ecologically benign and economically feasible medium for metal catalyzed reactions.[1] It has several advantages such as nonflammability, non-toxicity, absence of gas–liquid phase boundary and possible simplifications in work up. This makes the use of $ScCO_2$ as an attractive alternative to conventional organic solvents. Use of organometallic catalysts in $ScCO_2$ has already been well demonstrated in earlier studies.[2] Biphasic catalysis using the water soluble organometallic catalysts has widened the scope of homogeneous catalysis in practice as it gives easy separation of catalyst and reactants/products.[3] Hoechst AG is operating a 300 000 TPA plant on hydroformylation of propylene using Rh and a water-soluble phosphine complex in biphasic mode of operation. Considering the advantages of $ScCO_2$ as a reaction medium and water soluble metal complexes for catalyst-product separation, there is a need to combine these two approaches to develop truly environment-friendly processes. This approach also opens

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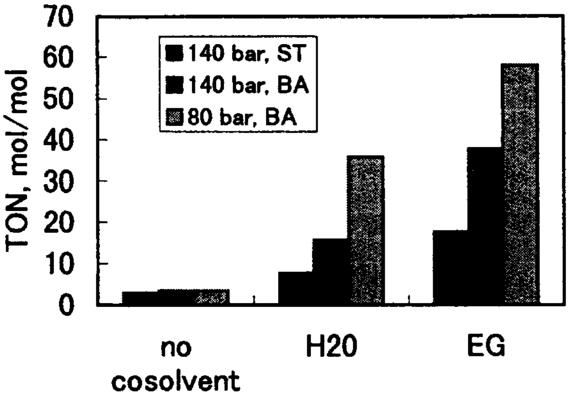

Figure 1. Effect of the addition of co-solvents on the rate of Heck vinylation of iodobenzene with butyl acrylate (BA) and styrene (ST) in $ScCO_2$. EG: ethylene glycol. Butyl acrylate or styrene: 10 mmol; iodobenzene: 10 mmol; triethylamine: 10 mmol; $Pd(OAc)_2$: 0.05 mmol; TPPTS: 0.2 mmol; water or EG: 1 ml; temperature: 60°C; time 17 h

up new avenues to carry out other homogeneously catalyzed reactions in $ScCO_2$ which have so far been limited due to solubility limitations of metal complexes in $ScCO_2$. In this paper, we will report Heck vinylation reactions using water-soluble catalysts in supercritical carbon dioxide as a medium.

2. Results and discussion

Recently, Carroll and Holmes[4] as well as Morita et al.[5] showed Heck and Stille coupling reactions using $ScCO_2$ as a reaction medium. They observed significantly lower conversions for conventional triphenylphosphine ligand due to its insolubility in $ScCO_2$. However, fluorinated phosphine ligands showed significantly higher conversions due to their higher solubility in $ScCO_2$. Similarly, Shezad et al.[6] showed that commercially available palladium sources containing fluorinated ligands are superior catalysts for Heck vinylation in $ScCO_2$. A heterogeneous Pd/C catalyst was also used in $ScCO_2$, but the reaction was found to be very slow and no data on leaching of Pd into the product were reported.[7] We have attempted Heck vinylation of iodobenzene (10 mmol) with butyl acrylate and styrene (10 mmol) in the presence of $ScCO_2$ at 80 bar and 140 bar. The reaction was carried out at 60°C for 17 hours using triethylamine (10 mmol) as a base. The results are presented in Fig. 1. $Pd(OAc)_2$ (0.05 mmol) and a water soluble analogue of triphenylphosphine ligand, TPPTS (triphenylphosphine trisulfonate sodium salt, 0.2 mmol), was used along with water or ethylene glycol (1 ml) as a co-solvent. In the absence of any co-solvents (i.e., in pure $ScCO_2$), the rates are very low; the catalyst remains insoluble (as observed by visual observations as described below) and it is very difficult to interact with reactants. However, the addition of a polar co-solvent like water, which can dissolve the catalyst, significantly increases the rate of reaction and a higher turnover number (TON) is observed. Many researchers report that the addition of such a co-solvent significantly enhances the solubility of substrates in $ScCO_2$.[8] When ethylene glycol was used as a co-solvent, further enhancement in the reaction rate was observed. This is mainly due to a comparably higher solubility of ethylene glycol in $ScCO_2$ than water.[9] These observations were consistent at two different pressures of carbon dioxide, 80 bar, just above the critical point and at 140 bar, under supercritical carbon dioxide. A higher TON has been observed at 80 bar than that at 140 bar.

Then, the effect of pressure on the Heck vinylation of iodobenzene with butyl acrylate has been investigated. Experiments were carried out in the range of 1–140 bar pressure of carbon dioxide. The results are shown in Table 1. It has been observed that with an increase in the pressure of carbon dioxide,

Table 1
Effect of CO_2 pressure on Pd-catalyzed Heck vinylation of iodobenzene with butyl acrylate in CO_2 with co-solvent at 60°C

Run No.	Solvent system	Pressure (bar)	Conversion# (%)	TON (mol/mol)	Selectivity to *trans*-product (%)	Pd leaching (ppm)
1	CO_2-EG	1	67.6	135.2	98.5	2.2
2	CO_2-EG	20	38.0	76.0	98.4	2.0
3	CO_2-EG	60	34.1	68.2	99.6	2.3
4	ScCO_2-EG	80	29.0	58.0	99.5	<0.1
5	ScCO_2-EG	100	22.3	44.6	100	<0.1
6	ScCO_2-EG	120	20.6	41.2	100	<0.1
7	ScCO_2-EG	140	18.9	37.8	99.2	<0.1
8	ScCO_2-H_2O	80	18.0	36.0	97.8	<0.1
9	ScCO_2-H_2O	140	8.0	16.0	100	<0.1

Butyl acrylate : 10 mmol; Iodobenzene : 10 mmol; Triethylamine: 10 mmol;
$Pd(OAc)_2$: 0.05 mmol; TPPTS: 0.2 mmol; Water or EG : 1 ml; Time: 17 hr.
Conversion is calculated based on the amount of iodobenzene consumed.

TON decreases near the critical point; however, there is a marginal decrease in TON once the supercritical stage is established, i.e., above 80 bar. It is important to note that the catalyst is stable at higher pressures above the critical point, below which significant leaching of Pd was observed to occur in the range of 2–3 ppm. After the reactions at higher pressures followed by phase separation by depressurization, pure reactants and products were obtained in an organic phase and the catalyst was obtained in the co-solvent phase. Then, the catalyst/co-solvent phase was used for further Heck reactions; similar conversion and selectivity were obtained during the additional three cycles.

The state of reaction system was examined through a high-pressure sapphire window of reactor at 60°C and at various pressures. It has been observed that, in the absence of co-solvent, the catalyst remains insoluble in the solvent, carbon dioxide, and thus lower conversions are obtained. All the organic reactants were observed to be soluble under the reaction conditions used. In the absence of co-solvents or at low pressures of carbon dioxide, the reaction system is very similar to biphasic ones reported recently by the present authors.[10] As the pressure was raised above the critical point, the volume of the catalyst-containing co-solvent phase was decreasing and the reaction seemed to take place in a single phase.

In conclusion, a $Pd(OAc)_2$/TPPTS catalyst system along with a co-solvent such as water or ethylene glycol is effective for Heck vinylation in supercritical carbon dioxide. In this system, the catalyst is so stable that no Pd leaching occurs, the reactants/products can be easily separated from the catalyst phase by depressurization and the catalyst can be easily recycled.

3. Experimental procedures

$Pd(OAc)_2$ (0.05 mmol) and TPPTS (0.2 mmol) were dissolved in ethylene glycol (1 ml) and iodobenzene, butyl acrylate and triethylamine in 10 mmol each were charged to a 50 ml preheated reactor (at 60°C). Liquid carbon dioxide was introduced into the reactor using a Jasco model 880-PU syringe pump through a 1/16 inch tube and check valve and compressed to the desired pressure. The pump delivered the CO_2 at a flow rate 3.5 ml/min. Pressure control was achieved by Jasco model 880-81 back pressure regulator. After reaction, the pressure was released through ethanol to collect residual charge dissolved.

Details of the reaction system and procedures used were previously described.[11] The products were analyzed using GC (Yanaco G3800, Silicone OV-1, 6m). The Pd leaching was examined using atomic absorption spectrometry as described earlier.[12] For recycle experiments, the reactor was depressurized after the completion of reaction. The reactor contains two phases, one phase containing reactants and products and the other phase (ethylene glycol) containing catalyst. The catalyst-containing phase was separated and mixed with fresh reactants (substrates and amine) for recycle studies.

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