Hydrocarboxylation of terminal alkenes in supercritical carbon dioxide using perfluorinated surfactants
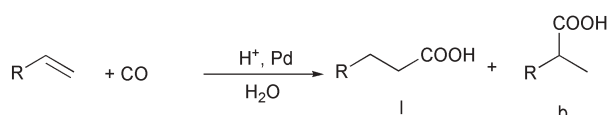
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High selectivity in acids is obtained in the first example of hydrocarboxylation of 1-octene in supercritical carbon dioxide using a Pd/P(4-C_6H_4-CF_3)$_3$ catalyst system and a perfluorinated surfactant.

Palladium-catalyzed hydrocarboxylation of alkenes (Scheme 1) is a straightforward and environmentally friendly method for obtaining carboxylic acids with an atom selectivity of 100%.[1] Carboxylic acids have important industrial applications. For instance, 2-arylpropionic acids are the most important class of non-steroidal anti-inflammatory drugs, and can be obtained by hydrocarboxylation of styrene.[2]

This reaction has been studied, reviewed and understood in organic solvents in the last decade.[3] One of the most important advances was the discovery that it can be performed in aqueous solutions using the water soluble Pd/TPPTS catalyst system (TPPTS = P(3-C_6H_4-SO_3Na)$_3$).[4,5] Other water-soluble catalyst systems have been studied since then.[6] Water is undoubtedly the greenest solvent for any chemical reaction. In aqueous systems, styrene and low terminal aliphatic olefins have been transformed with high conversion to the corresponding acids (TOF of up to 25 h^{-1} and 2500 h^{-1} were reported for styrene and 1-propene, respectively).[4,5] However, when higher α-olefins such as 1-hexene or 1-decene were hydrocarboxylated, the low mass transfer between the aqueous and organic phase, and double bond isomerization dramatically decrease the acid yield.[4] In these cases, mass transfer promoters such as cyclodextrins must be added to obtain selectivities up to 90%.[7]

Supercritical carbon dioxide (scCO$_2$) is an environmentally friendly substitute for organic solvents in metal-catalyzed reactions,[8,9] not only because of its benign character, but also because it often provides higher activities and selectivities[10] than organic or biphasic systems. Examples of this can be found in oxidation,[11] hydrogenation[12] or hydroformylation[13] reactions. Unfortunately, ionic and polar reagents are generally not very soluble in scCO$_2$, which restricts the application of scCO$_2$ in catalytic processes.[14] For example, water/scCO$_2$ multiphasic systems have been
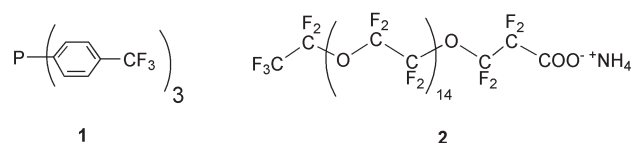

Fig. 1   Ligand **1** and perfluorinated surfactant **2**.

successfully used in the hydrogenation of cinnamaldehyde[15] and itaconic acid,[16] which have partial solubility in water, but these systems fail with low water-soluble substrates. To overcome this limitation, modified ligands such as perfluorinated phosphines or/ and soluble surfactants, which induce the formation of micelles with a high-density fluid phase, have been employed.[14] Perfluorinated surfactants are widely known for their ability to reduce interfacial tension and their high thermal and chemical stability. Water-in-carbon dioxide microemulsions (W/C) have been formed using ammonium carboxylate perfluoropolyether surfactants.[17] These dispersions have been used to solubilize hydrophilic substances into CO$_2$ and applied to organic reactions,[18] and to perform aqueous/scCO$_2$ biphasic metal-catalyzed reactions with water-soluble catalysts.[19]

Here we present the first example of the hydrocarboxylation of a terminal alkene (1-octene) in scCO$_2$. We used the scCO$_2$-soluble catalyst precursor [PdCl$_2$(PhCN)$_2$][20] associated with phosphine P(4-$C_6H_4CF_3$)$_3$ (**1**, Fig. 1) and a perfluorinated surfactant (the ammonium salt of Krytox® **2**, Fig. 1, M$_w$ = 1937 g mol^{-1}) as a stabilizer of the W/C dispersions. The catalyst will be at the scCO$_2$ phase and the water dispersion will facilitate the contact between the hydrophobic substrate and water.
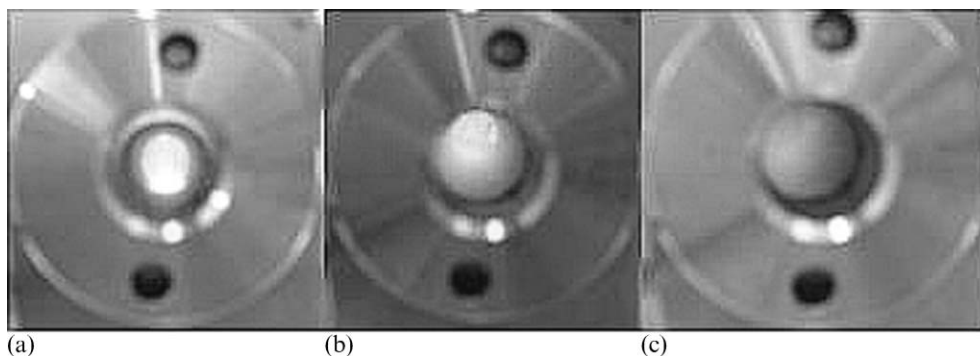
First, we examined the solubility of the Pd/**1** catalyst precursor in scCO$_2$. To do so, 0.1 mmol of [PdCl$_2$(PhCN)$_2$] and 0.4 mmol of

Scheme 1   Pd-catalyzed hydrocarboxylation of terminal alkenes.

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Table 1   Hydrocarboxylation of 1-octene using [PdCl$_2$(PhCN)$_2$]/**1**/**2** in scCO$_2$[a]

Entry	P_T(atm)	H$_2$O/**2**	%Conv.	%S$_a$	l/b
1	200	0	6	74	60/40
2	150	0	55	90	75/25
3[b]	30	0	78	63	68/32
4	150	28	80	80	80/20
5	150	14	93	77	82/18
6	150	7	79	81	89/11
7	165	14	44	80	78/22

[a] Reaction conditions: 1 mM Pd (0.025 mmol), P/Pd: 4, 12 h, P$_{CO}$: 30 atm, T: 90 °C, acid: oxalic acid (1.56 mmol); H$_2$O (12.5 mmol); Substrate: 1-octene (1.56 mmol); Phosphine: 0.1 mmol; Conv.: conversion; S$_a$: acid selectivity; l: linear acid, b: branched acid. **2** = Krytox®. [b] solvent: dimethoxyethane; ligand: PPh$_3$.

Fig. 2 Water–surfactant emulsion in supercritical conditions: a) $P < 100$ atm, $T = 70$ °C; b) 120 atm $< P <$ 150 atm, $T = 90$ °C; c) $P > 165$ atm, $T = 90$ °C.

1 were placed in a 100 ml autoclave equipped with sapphire windows, and the system was pressurized up to 30 atm of CO. Then, the pressure and temperature were gradually increased. At 180 atm and 70 °C a single yellow phase was formed.

Once the conditions in which the system became soluble had been determined, we performed the catalytic experiments using the *in situ* formed catalyst precursor [PdCl$_2$(PhCN)$_2$]/**1** (P/Pd = 4) in the presence of oxalic acid and added water.† The results are summarized in Table 1.

Conversion was very low (6%) at 90 °C and 200 atm of total pressure, although the system was soluble in these conditions (entry 1, Table 1). The chemoselectivity was also low and only 74% of the products were acids, the remaining products being the result of isomerization (2- and 3-octenes). Increases in conversion (up to 55%), selectivity (up to 90%) and regioselectivity in the linear isomer were observed when the total pressure was decreased to 150 atm (entry 2, Table 1). In these conditions visual inspection through the sapphire windows shows a suspension. When these results are compared with those obtained with [PdCl$_2$(PhCN)$_2$]/PPh$_3$ under the same conditions (entry 3, Table 1), it can be observed that there is a clear improvement in the selectivity if scCO$_2$ is used, although the conversion is lower. The selectivity obtained with our Pd/**1** system is better than the selectivity reported for aqueous biphasic catalysis with Pd/TPPTS. For instance, for 1-hexene 40% of isomerization was reported in the biphasic aqueous system.[4]

The fact that the conversion obtained was low was attributed to a mass transfer problem of the water to the scCO$_2$ phase. Thus, we decided to add an ammonium salt of perfluoropolyether carboxylic acid **2**[21] (Krytox®). We first examined the solubility of the [PdCl$_2$(PhCN)$_2$]/**1**/**2** system under scCO$_2$ (Fig. 2). To do so, 0.05 mmol of [PdCl$_2$(PhCN)$_2$], 0.20 mmol of **1**, 3.125 mmol of oxalic acid, 18.75 mmol of water and 1.78 mmol of **2** were placed in a 100 ml autoclave equipped with sapphire windows, and then the same method as for [PdCl$_2$(PhCN)$_2$]/**1** was followed. At 70 °C and below 100 atm, the scCO$_2$ phase was colorless and transparent (Fig. 2a). When the temperature and pressure were increased to 90 °C and 120 atm, respectively, we observed the formation of a suspension (Fig. 2b) that was white up to 165 atm and then turned yellow up to 180 atm (Fig. 2c)

The addition of surfactant **2** (H$_2$O/**2** = 28) to the Pd/**1** system increased both the conversion (entry 4, Table 1) and the regioselectivity to the linear acid to 80%. When the amount of **2**

was increased, the conversion reached a maximum of 93% at an H$_2$O/**2** ratio of 14 (entry 5, Table 1). In all these cases the selectivity in acids remained at 80% which is a better result than the one obtained with the organic and aqueous systems.[4] At higher pressure, when the system is soluble in scCO$_2$, the conversion decreased (44% conversion in entry 7, Table 1) as happened without the addition of surfactant.

Further experiments are in progress to optimize the parameters and obtain more information about the species formed under catalytic conditions.

In summary, we present the first example of the hydrocarboxylation of 1-octene in scCO$_2$ using the Pd/**1** catalyst precursor. The use of scCO$_2$ means that the selectivity in acids is higher than for the organic and aqueous systems. The addition of a perfluorinated surfactant enhances the activity and the regioselectivity to the linear acid although the selectivity decreases.

Notes and references

† Catalysis: [PdCl$_2$(PhCN)$_2$] (0.025 mmol) was mixed with 1.56 mmol of H$_2$C$_2$O$_4$·2H$_2$O, 0.1 mmol of **1** and **2** when used (mmol depending on the experiment according to Table 1). The mixture was loaded into a 25 ml stainless steel reactor vessel and the system was purged. Degassed water (0.23 ml), 1-octene (1.56 mmol) and undecane (0.13 ml) as GC internal standard were mixed and charged in vacuum. Then the CO gas was charged, the reactor pressurized to 30 atm, and the liquid carbon dioxide introduced. The contents were heated to 90 °C. The compressed carbon dioxide was introduced to attain the desired reaction pressure and magnetically stirred (750 rpm). After the reaction, the vessel was cooled with ice water to 0 °C and slowly depressurized to atmospheric pressure through a cold trap. The reaction mixture was extracted with diethyl ether and analyzed by gas chromatography.

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