New Sustainable Pd(II)/Fe(III) Catalytic System Very Efficient in the Hydromethoxycarbonylation of 1-octene

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Abstract

In order to increase the catalytic activity of the Pd(II)-complexes in the alcoxycarbonylation of 1-olefins, the presence in solution of a strong Brönsted acid together with a phosphine ligand is usually required. From an industrial point of view, such two additives, however, influenced the sustainability of the process mainly caused by the related corrosion of the reaction vessel and the toxicity of the phosphine ligand.

In this paper, the methoxycarbonylation of 1-octene has been efficiently carried out by using the $[Pd(TsO)_2(PPh_3)_2]/FeCl_3$ catalyst system. The catalyst is very active also without addition of PPh_3, reaching the TON of *ca.* 1300 (mol/mol) in 2 hours by using the Fe(III)/Pd(II) = 400/1 (mol/mol) system. Such value is higher than the values obtained by using the traditional strong Brönsted acid TsOH or other Lewis acid such as $AlCl_3$, in the presence of PPh_3. The reaction takes place with the formation of two isomeric products of linear and branched structures with a yield towards the linear isomer of *ca.* 80%.

Keywords

palladium catalyst, 1-octene, triphenylphosphine, carbon monoxide, hydromethoxycarbonylation, iron trichloride

1 Introduction

In the today's chemical industry, the esters of carboxylic acid are considered high value-added fine chemicals representing one of the most widely used chemical compound in the world [1–4]. Their simple but versatile chemistry is used in applications as diverse as food essence, pharmaceutics, plastics, resins, lubricants, paper, bio-fuel, in cosmetics and the personal care industry [1–15]. The industrial production is still mostly based on the Fisher reaction [16–20], but an interesting alternative is represented by the catalyzed hydroalkoxycarbonylation of olefins, a high versatile and atom-efficient reaction [21–30].
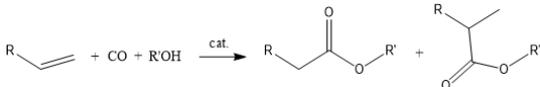
Although several transition metal complexes can be used as catalyst (Ru, Pd, Ni or Co complexes [23, 31–36]), the most promising appear the Pd(II) complexes, in terms of conversion, selectivity and process conditions, as to allow industrial applications. As an example of hydroalkoxycarbonylation, which has found industrial application, we can mention the Alpha process (developed by Lucite International) [37, 38], which produce methyl methacrylate through the reaction of formaldehyde with methylpropionate. The latter is produced, in the first step of such process, via hydromethoxycarbonylation of ethylene by using a Pd(II)-phosphine complex as catalyst precursor.

The choice of the phosphine ligand plays a fundamental role in determining the catalytic activity of the Pd(II)-complex, but the co-presence in solution of an excess of the same ligand and of a Brönsted acid, is almost always needed, in order to obtain the performance required. In fact, the appropriate acidic strength and the coordinative properties of the Brönsted acid (e.g., p-toluenesulfonic acid, TsOH) favor the in situ formation of active Pd-hydride species [26–29, 39, 40], whose decomposition to inactive Pd-metal is efficiently avoided by the presence in solution of the excess of the phosphine ligand (PPh_3) [9, 39–43] (see Scheme 1).

where L could be CO, PPh₃, solvent.
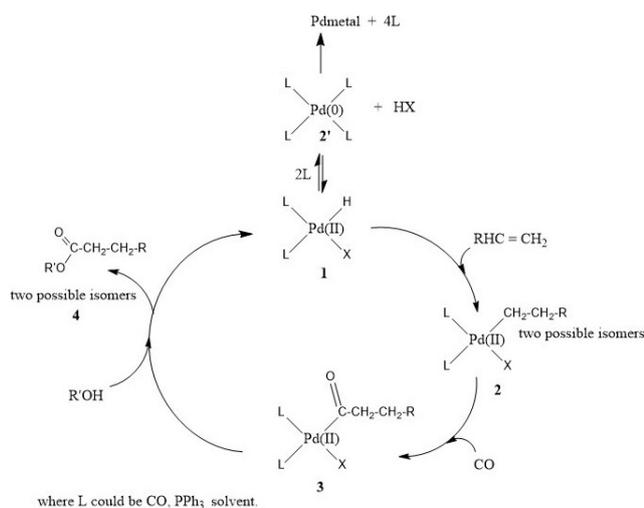
Scheme 1 Reaction mechanism widely accepted in literature

However, from an industrial point of view, we have also to consider the possible drawbacks and environmental impacts relate to such reaction. For instance, the use of hazardous chemicals and toxic solvents, the lack of substrate selectivity, excessive consumption of energy and possible corrosion of the equipment, which can influence the sustainability of the process [3, 4, 8, 9, 44]. Among these points, some attention should be paid to the addition of strong Brönsted acids, which could lead to corrosion problems in the reaction vessel and in the equipment, and to the addition of extra phosphine ligands, which could increase the toxic-related problems, e.g. in the food industry. To address such Brönsted acid related problems, the Lewis acids are increasingly used, as they have been shown to be effective for a variety of hydroalkoxycarbonylation protocols [45–49]. In this regard, in a previous paper, some of the authors have studied the effectiveness of $AlCl_3$ as substitute of the p-toluenesulfonic acid (TsOH) in the hydroethoxycarbonylation of 1-olefins [48–51].

In this paper the use of Lewis acids has been further investigated, funding that the $[Pd(TsO)_2(PPh_3)_2]/FeCl_3$ (TsO = p-tosylate) catalyst system led to the best results with 1-octene in methanol without adding toxic PPh₃. The use of cheap and very available $FeCl_3$, together with the absence of toxic PPh₃ in solution, represent an interesting result in terms of sustainability of the reaction. The comparison with TsOH and $AlCl_3$ has been also proposed and discussed.

2 Experimental
2.1 Reagents
The $[PdX_2(PPh_3)_2]$ complexes (see Table 1) were prepared as reported in literature [52–56] and characterized by FTIR and NMR analysis. Carbon monoxide and ethylene was supplied by SIAD Company Italy ('research grade', purity > 99.9%); Methanol, ethanol, propanol, P(p-MeOC₆H₄)₃, P(p-ClC₆H₄)₃, P(p-tolyl)₃, P(m-tolyl)₃, PPh₃, P(cyclohexyl)₃, PBu₃ and P(O-Ph)₃ were Aldrich/Merck products, used without further purification.

2.2 Equipments and characterization
The catalyst precursors have been weighted on a Sartorious Micro balance (precision 0.001 mg).

GC/MS analyses were performed on a MS Agilent apparatus 5975C Model, interfaced with an Agilent chromatograph 7890 A Model equipped with a HP5 column (30 m × 0.25 mm × 0.25 μm, oven: 318 K (3 min) to 523 K at 15 K/min).

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet Magna 750 instrument in KBr powder. All the NMR spectra were recorded on a Bruker Avance 300 spectrometer.

2.3 Catalytic reactions
The catalysis has been carried out in a batch reactor of ca. 60 mL provided with a magnetic stirrer. In a typical experiment, 1.50 10^{-3} mmol of Pd(II) complex (for instance 1.46 mg of $[Pd(TsO)_2(PPh_3)_2]$), together with the excess of triphenylphosphine (PPh₃) and the acid in a molar ratio Pd(II)/PPh₃/AlCl₃ = 1/12/100 (mol/mol/mol)) were added to 20 mL of solvent (methanol). In order to avoid catalyst deactivation, due to the presence of air, the reactor was carefully flushed with CO at room temperature with stirring. The reactor was then heated up to 393 K in ca. 10 min without stirring under a 0.5 MPa of CO pressure. At 393 K the pressure has been then adjusted to the desired value (typically 5.0 MPa of CO) and, while stirring, maintained constant by continuously supplying the CO from a reservoir throughout the experiment (for instance 3 h). At the end of the experiment, the reactor was quickly cooled and carefully depressurized at room temperature.

The reaction products have been detected and quantified by the GC and GC-MS analysis.

All the experiments have been repeated at least twice and the error analysis confirmed the reproducibility of the data with an error of ±1%.

3 Results and discussion
3.1 Preliminary tests
The hydromethoxycarbonylation of some 1-olefins has been carried out in the preliminary tests by using the catalyst system $[Pd(AcO)_2(PPh_3)_2]/[PPh_3]/acid$ = 1/12/100 (mol/mol/mol) [52, 53]. Table 1 (entries 1–5) shows that the Lewis acid ($AlCl_3$) is not active toward the

hydromethoxycarbonylation of ethylene and propylene, whereas it leads to the best conversion of 1-octene and 1-decene (ca. 80 % molar conversion).

Therefore, focusing on 1-octene, we have tested the influence of different Lewis acids (Table 1 entries 7–14) in comparison to TsOH (entry 6). Among these, the $FeCl_3$ leads to an interesting result both in terms of conversion and yield to linear ester (74% of conversion; 75% of linear esters; entry 9), also considering that it is cheap and very available.

Moreover, the yield to linear isomer obtained with the $[Pd(TsO)_2(PPh_3)_2]/FeCl_3/PPh_3$ catalyst system (Table 1, entry 4) is similar to the values reported in the literature [50, 51]. According to literature, Table 2 shows that the weakly coordinating ligands lead to the best catalytic activity (Table 2 entries 1–4). In addition the influence of different phosphine ligands, in terms of relative nucleophilicity and steric properties, have been also tested substituting the phosphine in both the Pd(II) complex and in the solution as excess (Table 2 entries 5–10).

The results confirm that the optimum combination of the stereo-electronic effects are obtained with PPh_3, according to the conclusion that more basic ligands disfavors the coordination of the nucleophilic alkene to the metal centre, while with the less basic phosphines the alkene binds too strongly to the metal disfavoring the catalysis.

Table 1 Lewis acids tested in the hydromethoxycarbonylation of 1-octene

Entry number	Co-cat.	Olefin	Conv.* (%)	Linear ester (%)
1	$AlCl_3$	Ethene[a]	n.d.	/
2	$AlCl_3$	Propene[a]	trace	/
3	$AlCl_3$	1-hexene	30	65
4	$AlCl_3$	1-octene	80	68
5	$AlCl_3$	1-decene	78	60
6	TsOH	1-octene	95	80
7	$SnCl_2$	1-octene	20	75
8	$YbOTf_3$	1-octene	22	80
9	$FeCl_3$	1-octene	74	75
10	$InCl_3$	1-octene	23	60
11	$LaCl_3$	1-octene	58	63
12	$PrCl_3$	1-octene	77	65
13	$YbCl_3$	1-octene	61	60
14	$SmCl_3$	1-octene	73	61

Run conditions: $[Pd(OAc)_2(PPh_3)_2]$ = $1.50 \cdot 10^{-3}$ mmol (1.87 mg), Pd(II)/PPh_3/$AlCl_3$ = 1/12/100 (mol/mol/mol), solvent = MeOH, V_{tot} = 20 mL, olefin/Pd(II) = 2000/1 (mol/mol), T = 393 K, P_{tot} = 5.0 MPa (CO), reaction time = 5 h.
* Selectivity to esters, sum of branched and linear for entries 3–14 > 99 molar %.
[a] Added as gas = 0.5 MPa (in this case CO was 4.5 MPa).

Table 2 Influence of different Pd(II) precursor in the hydromethoxycarbonylation of 1-octene

Entry number	Catalyst precursor	TON[a] (mol/mol)	Linear esther (mol %)
1	$[PdCl_2(PPh_3)_2]$	520	70
2	$[Pd(AcO)_2(PPh_3)_2]$	610	75
3	$[PdBr_2(PPh_3)_2]$	627	73
4	$[Pd(TsO)_2(PPh_3)_2]$	630	80
5	$[PdCl_2[P(o\text{-tolyl})_3]_2]$	125	26
6	$[PdCl_2[P(o\text{-MeOPh})_3]_2]$	32	22
7	$[PdCl_2[P(m\text{-tolyl})_3]_2]$	520	55
8	$[PdCl_2(PCy_3)_2]$	12	71
9	$[PdCl_2(P(p\text{-tolyl})_3)_2]$	500	70
10	$[PdCl_2(P(p\text{-F-Ph})_3)_2]$	485	66

Run conditions: Pd(II) = $1.50 \cdot 10^{-3}$ mmol, Pd(II)/$P(PhX^*)_3$/$FeCl_3$ = 1/12/100 (mol/mol/mol), V_{tot} = 20 mL, 1-octene/Pd(II) = 2000/1 (mol/mol), solvent = MeOH, V_{tot} = 20 mL, T = 393 K, P_{tot} = 5.0 MPa (CO), reaction time = 2 h.
* Phosphines used in the relative complexes as ligand.
[a] Selectivity to esters (sum of branched and linear) > 99 % molar.

On the basis of these results the catalytic activity of the $[Pd(TsO)_2(PPh_3)_2]/FeCl_3/PPh_3$ system has been further investigated.

3.2 On the catalytic activity of the $[Pd(TsO)_2(PPh_3)_2]/FeCl_3/PPh_3$ system

The Fig. 1 shows the influence on the catalytic activity of $FeCl_3$ concentrations, compared to TsOH and $AlCl_3$. In all the cases, the addition of a co-catalyst is needed and the catalytic activity linearly increases by increasing the co-catalyst/Pd molar ratio following similar trends, even if some differences can be highlighted. For instance, at low concentration (co-catalyst/Pd = 10/1 mol/mol), the more efficient was TsOH (TON = 650 moles of esters/moles of Pd) respect to $AlCl_3$ (TON = 542) and $FeCl_3$ (TON = 466). On the other hand, at high concentration (co-catalyst/Pd > 400/1 mol/mol), the $FeCl_3$ led to the best performance (TON = 1200 moles of esters/moles of Pd) compared to TsOH (TON = 1150) and $AlCl_3$ (TON = 1100).

3.3 Influence of the addition of PPh_3

The PPh_3/Pd molar ratio was also found to have a significant role in catalytic activity. The main role of PPh_3, added to the $[Pd(TsO)_2(PPh_3)_2]$ catalyst, is to avoid the formation and the precipitation of inactive Pd metal (see introduction [26, 27, 41], increasing therefore the catalyst performance. According to this, the Fig. 2 shows that, in the presence of TsOH, the TON increases with the PPh_3 concentration, reaching a plateau value of *ca.* 800 (mol/mol) at PPh_3/Pd >8/1.
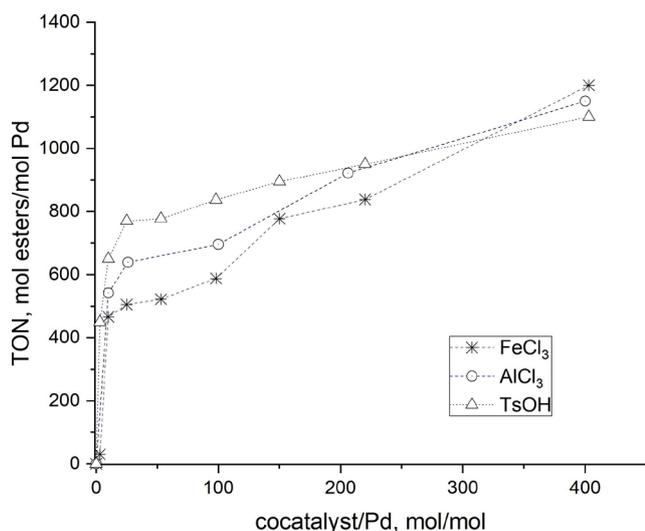
Fig. 1 Influence of co-catalyst on TON

Run conditions: $[Pd(TsO)_2(PPh_3)_2] = 1.50 \cdot 10^{-3}$ mmol (1.46 mg), Pd(II)/$PPh_3 = 1/12$ (mol/mol), $V_{tot} = 20$ mL, 1-octene/Pd(II) = 2000/1 (mol/mol), solvent = methanol, $T = 393$ K, $P_{tot} = 5.0$ MPa (CO), reaction time = 2 h.
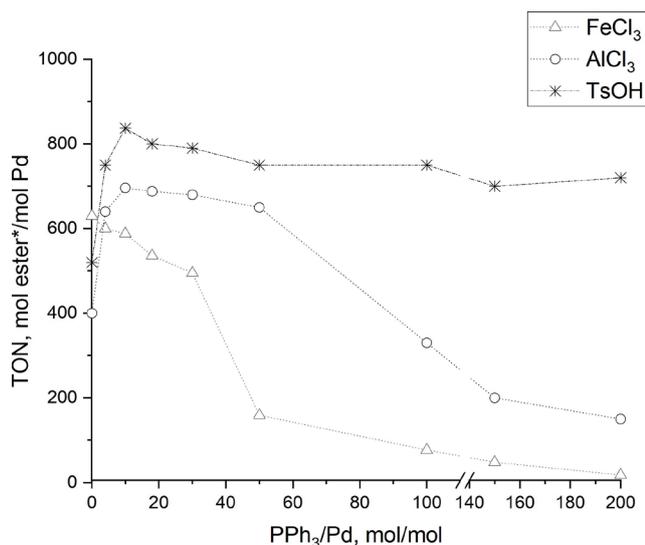
Fig. 2 Influence of PPh_3/Pd molar ratio on TON

Run conditions: $[Pd(TsO)_2(PPh_3)_2] = 1.50 \cdot 10^{-3}$ mmol (1.46 mg), Pd(II)/$FeCl_3 = 1/100$ (mol/mol), $V_{tot} = 20$ mL, 1-octene/Pd(II) = 2000/1 (mol/mol), solvent = methanol, $T = 393$ K, $P_{tot} = 5.0$ MPa (CO), reaction time = 2 h.
* PPh_3 added in solution

However, by using $AlCl_3$ instead of TsOH, the TON increases up to a maximum value of *ca.* 700 (mol/mol) at PPh_3/Pd higher than 12/1 (mol/mol), after then it quickly decreases for PPh_3/Pd > 100/1 (mol/mol).

On the contrary, by using $FeCl_3$, the TON linearly decreases by increasing the PPh_3/Pd molar ratio, throughout the range studied. This suggests that the increase of the PPh_3 concentration favors the formation of phosphine complexes also with Fe [56–60], which probably are less

or not active as co-catalysts. According to this, the Fig. 2 shows that $FeCl_3$ was more active in absence of PPh_3, leading to a TON of 630 (mol/mol). Such TON can by readily increases by increasing the $FeCl_3$/Pd molar ratio, reaching for instance *ca.*1300 (mol/mol) by using the $FeCl_3$/Pd = 400/1 (mol/mol).

In all the experiments in Figs. 1 and 2, no by-products were detected (selectivity to esters >99%) having a yield to linear ester of 80–82%, by using $FeCl_3$ and TsOH, and 65–70% by using $AlCl_3$.

3.4 On the reaction mechanism

Although the mechanism of hydroalcoxycarbonylation of olefins in the presence of Brönsted acid is widely studied in the literature, we can do some supposition on the role played by $FeCl_3$ as substituted of the Brönsted acid. Under the reaction conditions, the tosylate ligands in the Pd(II) precursor (weakly coordinating) are readily substituted by the solvent forming a cationic complex in which they are the counter-anions [42] (a in Scheme 2). The active species for the hydromethoxycarbonylation (b and c in Scheme 2), can easily form through reactions 2 and 3. Species b and c start two possible cycles to form the esters (isomers) together with the active species, which restart a new cycle. However, it is widely reported that the redox deactivation of the Pd(II) active species can readily occur forming less/not active Pd(0) species or Pd metal [42], with a consequent progressive decrease of the catalytic activity in the absence of an excess of Brönsted acid. Therefore, in light of the results reported In the present manuscript, it is plausible to suppose that the addition of $FeCl_3$ forms a redox couple with Pd(0), which gives Pd(II) active species again [61] (Scheme 2, reaction 5). Therefore the catalysis occurs without formal reduction to Pd(0) during the catalytic cycle (fast
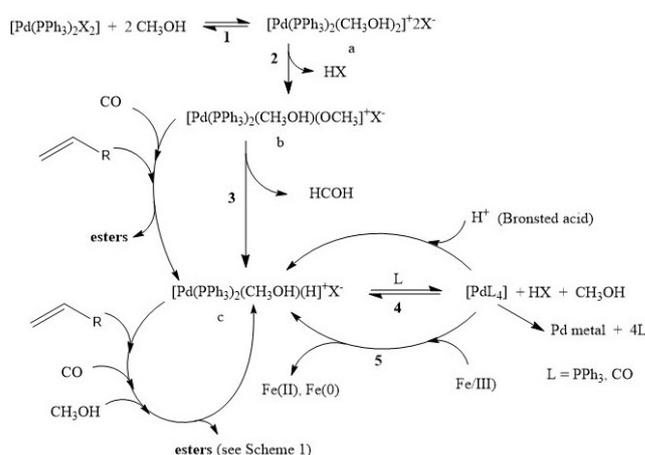
Scheme 2 Proposed reaction mechanism

reaction) so that it is no longer necessary to add the excess of PPh_3 to stabilize in solution the Pd(0) complexes as in the presence of Brönsted acid. Furthermore, it is widely reported that some Lewis acids could polarize the O–H bond of alcohols, which possibly provides the source of the [Pd-H] and/or [Pd-OR] species to initiate and sustain the catalytic cycle in Scheme 2 [47–50]

4 Conclusion

The $FeCl_3$ results an effective and interesting substitute of the *p*-toluenesulfonic acid and $AlCl_3$ as promoter for the hydromethoxycarbonylation of 1-octene. The reaction takes place with the formation of two isomeric products of linear and branched structures without by-products. Under the best reaction conditions tested, the TON (sum of isomeric esters of linear and branched structures) reaches a value of *ca.*1300 (mol/mol) by using the $FeCl_3/Pd = 400/1$ molar ratio, with a yield towards the linear isomer of *ca.* 80 %. Furthermore, the use of $FeCl_3$ as co-catalyst allows to carry out the phosphine-free reaction, avoiding the toxicity related problems.

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