

Effect of a hydride source (water, hydrogen, *p*-toluenesulfonic acid) on the hydroesterification of ethylene to methyl propionate using a $\text{Pd}(\text{PPh}_3)_2(\text{TsO})_2$ ($\text{TsO} = p$ -toluenesulfonate anion) catalyst precursor

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Abstract

Hydroesterification of ethylene to methyl propionate has been studied using the catalyst precursor $\text{Pd}(\text{PPh}_3)_2(\text{TsO})_2$, which is active in presence of PPh_3 and TsOH ($\text{TOF} = 5700 \text{ h}^{-1}$ at 120°C , 40 atm ($\text{CO}/\text{C}_2\text{H}_4 = 1/1$), $\text{Pd}/\text{PPh}_3/\text{TsOH} = 1/8/10$, $[\text{Pd}] = 2 \times 10^{-3} \text{ mol l}^{-1}$, solvent methanol, $\text{H}_2\text{O} = 800 \text{ ppm}$). In this paper we study the promoting effect of a hydride source, molecular hydrogen, water and *p*-toluenesulfonic acid (TsOH) and the inhibiting effect of *p*-benzoquinone. On the basis of experimental evidences, of the two possible initial steps of the catalytic cycle, the insertion of the olefin into a Pd-H species or into a Pd-OCH_3 species, it is suggested that the first plays a more important role. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Hydroesterification; Ethylene; Carbon monoxide; Palladium; Catalyst

1. Introduction

Pd -catalyzed carbonylation of ethylene results in the formation of industrially important products, such as propionic acid [1–4], its ester [5–13], diethylketone [14] and $\text{CO-C}_2\text{H}_4$ copolymers [15–19]. Carboxylic acid esters are known as industrial chemicals since many years and large amounts are used in the manufacture of several products. In particular, alkyl propionates are of interest as solvents, flavourings and perfumes.

Particularly interesting are the results obtained with the catalyst formed in situ by the combination of palladium acetate, triphenylphosphine and an acid whose anion is weakly coordinating [9], so that the metal cation has easily available coordination sites capable of activating the reacting molecules. Using *p*-toluenesulfonic acid (TsOH) and the catalyst precursor in the ratio $\text{Pd}/\text{PPh}_3/\text{TsOH} = 1/30/20$, under a pressure of 45 atm ($\text{CO}/\text{C}_2\text{H}_4 = 1/1$ molar ratio) and at 115°C , methylpropionate is obtained with a TOF of 5000 h^{-1} ($\text{TOF} = \text{mol of ester/mol of Pd-H}$) and a selectivity higher than 98% [9].

It has been observed that when the catalyst is formed in situ the acetate complex transforms mainly into $\text{Pd}(\text{PPh}_3)_2(\text{TsO})_2$ [20]. Since the in situ procedure can cause a loss of activity due to the fast reduction

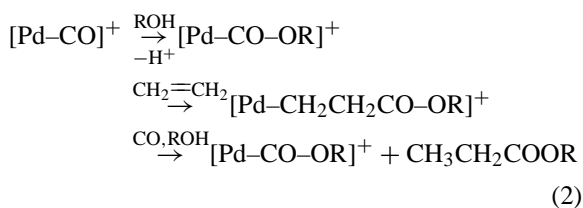
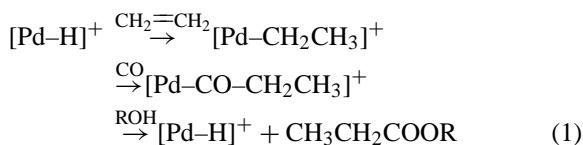
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of Pd(II) to inactive palladium metal and since Pd(OAc)₂, PPh₃ and TsOH promptly react to give Pd(PPh₃)₂(TsO)₂ (**I**), which is more easy to handle. In the present study we employed this last complex as catalyst precursor.

It is widely accepted that the catalytic cycle starts from the insertion of the olefin into a Pd–H or a Pd–COOCH₃ species:



The Pd–hydride species forms from the precursor and a hydrogen source [21–23], while the Pd–carboalkoxy species forms by interaction of a Pd–carbonyl species with the alkanol [23–25]. We found that hydrogen, water, and TsOH, which can act as Pd–hydride source, have a promoting effect on the catalytic system, while *p*-benzoquinone, that may favour the formation of the Pd–carbomethoxy species, has an inhibiting effect. These findings suggest that Pd–H species plays a key role in the catalytic cycle.

2. Results and discussion

2.1. On the catalyst

The catalyst precursor **I** is highly active in reaction (3) only in the presence of an additional amount of

PPh₃ and TsOH.

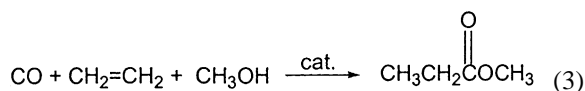
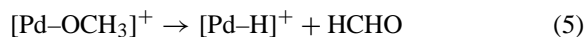
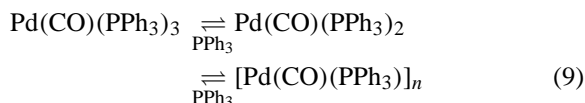
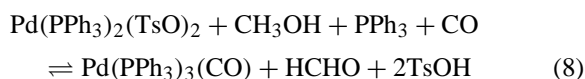


Table 1 shows that complex **I**, under the reaction conditions specified, does not catalyze reaction (3), being decomposed to inactive Pd metal.

This fact suggests that if there was formation of the active Pd–hydride or a Pd–methoxy species, for instance by reaction with the solvent (reactions 4 and 5), they decomposed to Pd metal before starting the catalytic cycle (reactions 6 and 7), even in the presence of TsOH (Table 1, entry 2).



The addition of PPh₃ ligand avoids the precipitation of Pd metal (Table 1, entry 3). However, in the absence of TsOH, the starting precursor **I** is reduced to the inactive Pd(0) complex Pd(CO)(PPh₃)₃ (**II**) (or [Pd(CO)(PPh₃)₃]_{*n*} (**III**)), probably via reactions (8) and (9), as shown by the IR spectra of the solid recovered after the catalysis is attempted [26,27].



Catalytic activity is observed (Table 1, entry 4) only when PPh₃ is used with TsOH, probably preventing

Table 1

Entry (no.)	Complex ^a	Pd(II) (mmol)	PPh ₃ (mmol)	TsOH (mmol)	time (h)	PrOMe (mol/molPd/h)	Pd _{met}
1	Pd(PPh ₃) ₂ (TsO) ₂	0.1	–	–	4	–	yes
2	Pd(PPh ₃) ₂ (TsO) ₂	0.1	–	1	5	–	yes
3	Pd(PPh ₃) ₂ (TsO) ₂	0.1	1	0	5	–	no
4	Pd(PPh ₃) ₂ (TsO) ₂	0.1	0.4	0.5	5	600	no

^a Run conditions: *T* = 90°C, *P* = 50 atm (CO/C₂H₄ = 1/1), MeOH = 50 ml, H₂O = 200 ppm.

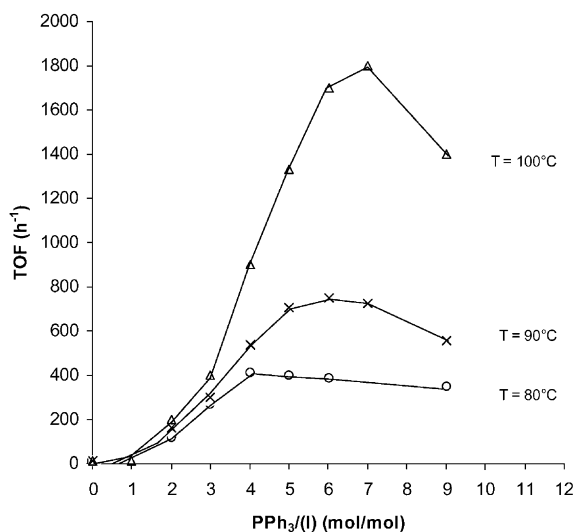


Fig. 1. Effect of PPh_3/I molar ratio on the TOF. Run conditions: $\text{Pd}(\text{PPh}_3)_2(\text{TsO})_2(\text{I}) = 0.1 \text{ mmol}$; $\text{I}/\text{TsOH} = 1/8$; methanol = 50 ml; $\text{H}_2\text{O} = 800 \text{ ppm}$, $P_{\text{tot}} = 40 \text{ atm}$ ($\text{CO}/\text{C}_2\text{H}_4 = 1/1$); reaction time = 1 h.

reaction (6)–(8) to be shifted to the right, or reoxidating reduced palladium to a Pd–H, thus acting as a hydride source, here schematized by reaction (10):

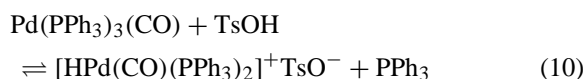


Fig. 1 shows the TOF as function of PPh_3/I at different temperatures and using a constant $\text{TsOH}/\text{I} = 8/1$ ratio. At each temperature, the TOF passes through a maximum whereupon it decreases probably because PPh_3 competes for the coordination of the reacting molecules and/or it shifts to the left equilibrium (10), decreasing the concentration of the active Pd–hydride species.

2.2. Effect of the run conditions on TOF

2.2.1. Effect of pressure

The effect of pressure has been studied using a constant temperature of 100°C and a constant $\text{CO}/\text{C}_2\text{H}_4$ molar ratio (1/1). Fig. 2 shows that the TOF passes through a maximum upon increasing the total pressure. Since the highest catalytic activity is observed under 40 atm of total pressure, all the other experiments have been carried out under this pressure.

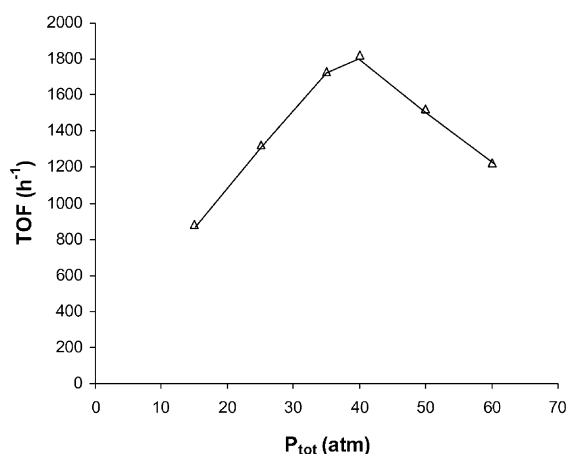


Fig. 2. Effect of the total pressure on the TOF. Run conditions: $\text{Pd}(\text{PPh}_3)_2(\text{TsO})_2(\text{I}) = 0.1 \text{ mmol}$; $\text{I}/\text{PPh}_3/\text{TsOH} = 1/6/8$; methanol = 50 ml; $\text{H}_2\text{O} = 800 \text{ ppm}$; $T = 100^\circ\text{C}$; reaction time = 1 h.

2.2.2. Effect of temperature

The Fig. 3 shows that the TOF increases upon increasing the temperature. Using the catalyst system in the ratio $\text{I}/\text{PPh}_3/\text{TsOH} = 1/6/8$, and under a total pressure of 40 atm, at 120°C a TOF of 5700 h^{-1} is reached. However, above 100°C the catalyst partially decomposes to Pd metal. Thus all the experiments described hereafter have been carried out up this temperature.

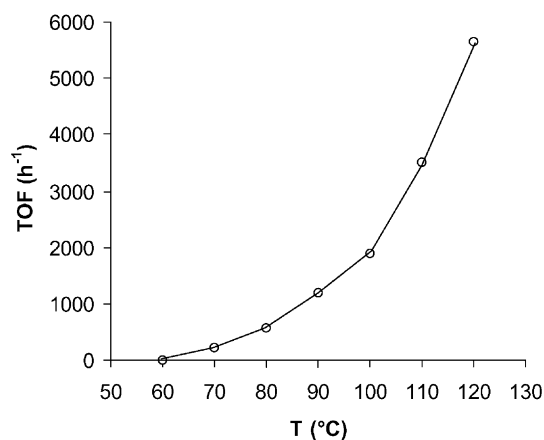


Fig. 3. Effect of the temperature on the TOF. Run conditions: $\text{Pd}(\text{PPh}_3)_2(\text{TsO})_2(\text{I}) = 0.1 \text{ mmol}$; $\text{I}/\text{PPh}_3/\text{TsOH} = 1/6/8$; methanol = 50 ml; $\text{H}_2\text{O} = 800 \text{ ppm}$; $P_{\text{tot}} = 40 \text{ atm}$; reaction time = 1 h.

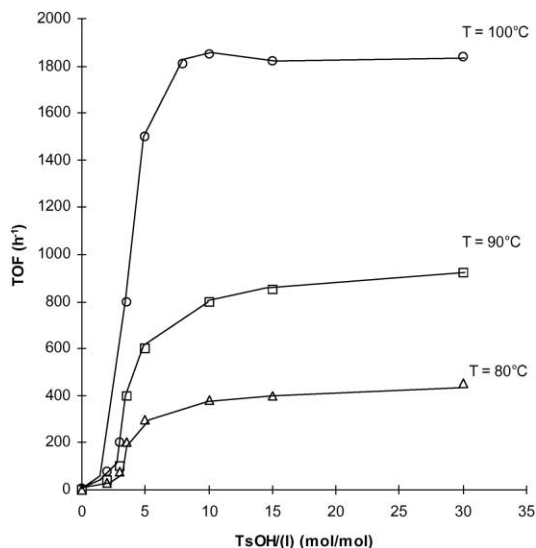


Fig. 4. Effect of TsOH/I molar ratio on the TOF. Run conditions: Pd(PPh₃)₂(TsO)₂(**I**) = 0.1 mmol; **I**/PPh₃ = 1/6; methanol = 50 ml, H₂O = 100 ppm, P_{tot} = 40 atm (CO/C₂H₄ = 1/1); reaction time = 1 h.

2.3. Effect of a hydride source on the TOF

2.3.1. Effect of *p*-toluenesulfonic acid

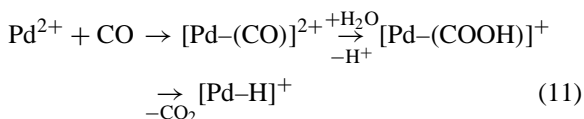
The Fig. 4 shows the effect of the TsOH/**I** molar ratio on the TOF at different temperatures up to 100°C.

It is interesting to note that the promoting effect of the acid is significant even in the presence of slight amounts of acid (TsOH/**I** = 2/1).

At all temperatures, using a PPh₃/**I** = 6/1, the TOF reaches a plateau (ca. 1750 mol PrOMe/mol Pd–H) at TsOH/**I** = 5/1. As already mentioned, it is likely that the acid prevent the formation of inactive reduced palladium species (reactions (6)–(8), (10)).

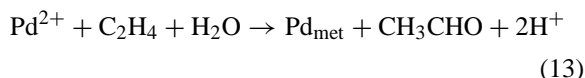
2.3.2. Effect of the water

It is known that water can act as a source of hydride species through a reaction strictly related to the water gas shift reaction (reaction (11)) [14,21,28].



Upon addition of increasing amounts of water (up to 5000 ppm) to the solvent, in absence of acid (PPh₃/**I** =

6/1), no catalytic activity is observed. The precursor decomposes to inactive palladium metal, probably through reactions here schematized:



Only in the presence of the acid, precursor **I** is active. In order to evidentiare a possible effect of water as hydride source, we carried out experiments in the presence of an amount of acid just enough to promote the catalytic activity of **I**.

The Fig. 5 shows, at different temperatures, the effect of water on the TOF using the system **I**/PPh₃/TsOH in the ratio 1/6/1. At 100°C the TOF reaches a maximum (1500 h⁻¹) at about 800 ppm of water. It is reasonable to suppose that water favours the formation of Pd–H species in cooperation with TsOH (reactions (11), (6)–(8), (10)). A further increase of water reduces the TOF drastically. It is likely the water competes with the coordination of ethylene and carbon monoxide, slowing down the insertion of the olefin into a Pd–H species. Under

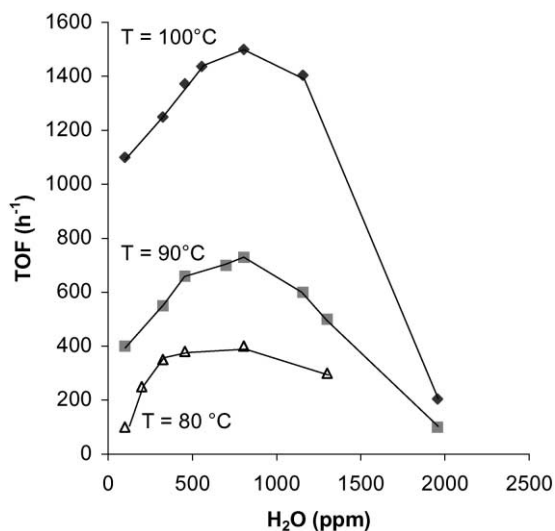


Fig. 5. Effect of water on the TOF. Run conditions: Pd(PPh₃)₂(TsO)₂(**I**) = 0.1 mmol; **I**/PPh₃/TsOH = 1/6/1, methanol = 50 ml; P_{tot} = 40 atm (CO/C₂H₄ = 1/1); reaction time = 1 h.

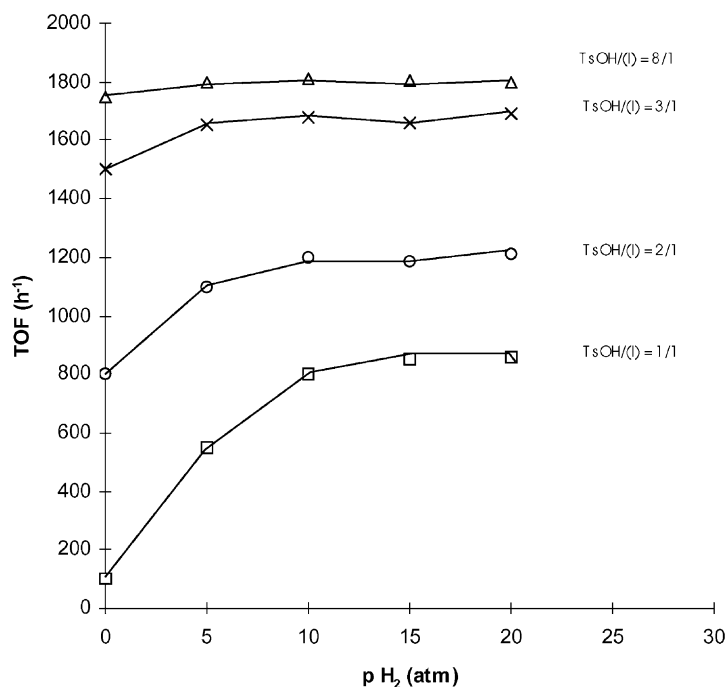


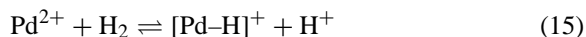
Fig. 6. Effect of partial pressure of hydrogen on the TOF at different TsOH/I ratios. Run conditions: Pd(PPh₃)₂(TsO)₂(I) = 0.1 mmol; I/PPh₃ = 1/6; methanol: 50 ml; H₂O < 100 ppm (addition of 1% of TMO as water scavenger); P_{tot} = 30 atm (CO/C₂H₄ = 1/1); T = 100°C; reaction time = 15 min.

these conditions decomposition of the hydride to the reduced palladium may be favoured:



2.3.3. Effect of hydrogen

Hydrogen can also act as hydride source:



The Fig. 6 shows the effect of hydrogen, at different TsOH/I ratios, on the TOF in experiments carried out in the presence of trimethyl orthoformate as water scavenger. The promoting effect of hydrogen is more evident the lower this ratio is.

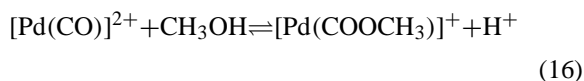
The Fig. 7 shows the effect of hydrogen at different temperatures using a PPh₃/I ratio of 6/1. Even at 80°C the effect of hydrogen is significant. Note, however, in the presence of hydrogen fast deactivation of the catalyst (Pd metal formation) occurs even just after 15–30 min.

Data reported in Figs. 6 and 7 refer to a reaction time of 15 min. It should be added that in the presence of hydrogen there is formation of ethane.

2.4. On the mechanism of the catalytic cycle

Scheme 1 schematizes the two cycles proposed. Cycle (1) starts from a Pd–H species. On the basis of the promoting effect of a hydride source such as TsOH, water or hydrogen, it is likely that this mechanism plays a major role.

Mechanism 2 may also be operative, however not in the case when an excess of TsOH is used because equilibrium (16) is reversed toward the left [29].



That 2 is not the main mechanism to be operative is also suggested by the results observed carrying out

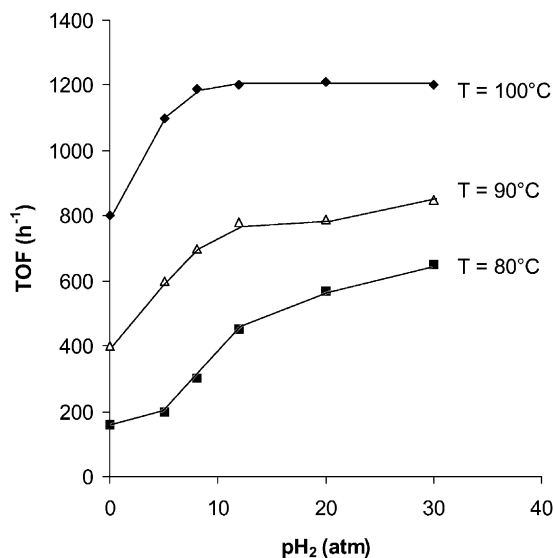
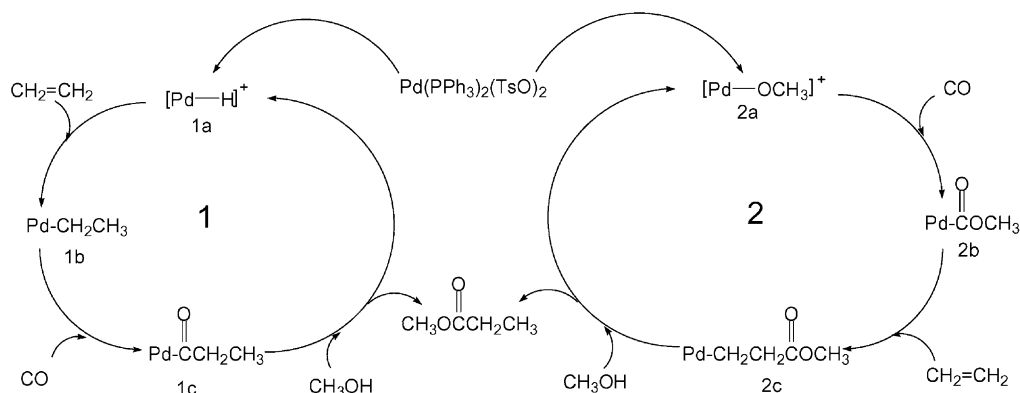
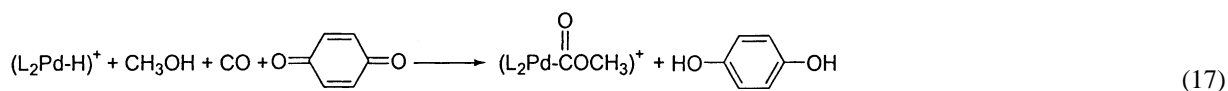


Fig. 7. Effect of partial pressure of hydrogen on the TOF at different temperatures. Run conditions: Pd(PPh₃)₂(TsO)₂ (I) = 0.1 mmol; I/PPh₃/TsOH = 1/6/1; methanol: 50 ml; H₂O = 100 ppm; P_{tot} = 30 atm (CO/C₂H₄ = 1/1); reaction time = 15 min.

experiments in the presence of *p*-benzoquinone (BQ) [I/PPh₃/TsOH/BQ = 1/6/8/50], as BQ promotes the formation of a Pd–COOCH₃ species at the expense of a Pd–H species [19,21]:



Scheme 1. Proposed catalytic cycles.

3. Experimental section

3.1. Materials

Carbon monoxide and ethylene (purity higher than 99%) were supplied by SIAD Spa (Italy). Pd(OAc)₂ 98%, triphenylphosphine and *p*-toluenesulfonic acid were purchased from Aldrich. Pd(PPh₃)₂(TsO)₂ complex was prepared according to the method reported in literature [20].

3.2. Experimental set-up

All the experiments were carried out in a stainless steel autoclave of ca. 250 cm³ of capacity, provided with a mechanical stirrer. The reaction occurred in a ca. 150 ml Pyrex glass beaker placed into the autoclave in order to prevent contamination by metallic species because of corrosion of the internal surface of the autoclave.

Carbon monoxide and ethylene were supplied from a gas reservoir connected to the autoclave through a constant pressure regulator. The autoclave was provided with a temperature control ($\pm 0.5^\circ\text{C}$) and a sampling of gas phase.

In order to establish whether diffusion of the gases controls the rate of reaction (3), experiments were

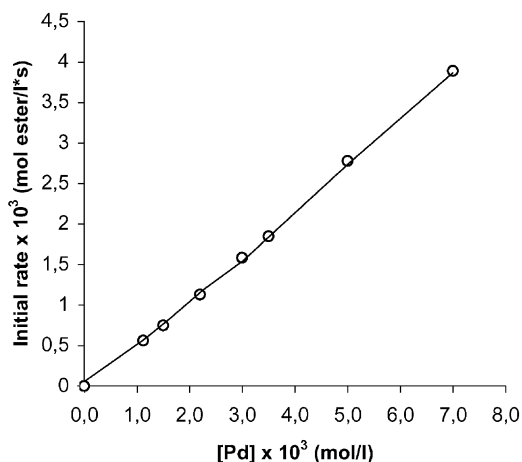


Fig. 8. Effect of catalyst loading on the initial rate. Run conditions: Pd(PPh₃)₂(TsO)₂ (**I**) = 0.1 mmol; I/PPh₃/TsOH = 1/6/8; methanol: 50 ml; H₂O = 800 ppm; P_{tot} = 40 atm (CO/C₂H₄ = 1/1); T = 100°C; stirrer speed = 700 rpm; reaction time = 1 h.

carried out with increasing amount of catalyst under the condition specified in Fig. 8, which allows high reaction rates. It can be seen that up to a concentration of the catalyst [Pd] = 7 × 10⁻³ mol l⁻¹ the diffusion of the gases is faster than the reaction rate. All the results reported in the table and in the figures, are related to a catalyst concentration of [Pd] = 2 × 10⁻³ mol l⁻¹.

The apparent activation energy obtained from the Arrhenius plot of the data in Fig. 3 (19 kcal/mol) and the negligible effect of the agitation speed variation, beyond 500 rpm (500–1000 rpm), on the TOF, indicates that gas-diffusion does not control the reaction.

3.3. Experimental procedure

Typical reaction conditions were: T = 100°C, P = 40 atm (CO/C₂H₄ = 1/1 molar ratio), Pd(PPh₃)₂(TsO)₂ = 0.1 mmol, reaction time 1 h. Triphenylphosphine and *p*-toluenesulfonic acid was also added to the reaction mixture so that total molar ratio was I/PPh₃/TsOH = 1/6/8.

In a typical experiment, known quantities of **I**, PPh₃ and TsOH along with 50 ml of solvent (methanol)

where charged into the glass bottle placed in the autoclave. Then, the autoclave was pressurized (P_{tot} < 5 atm) at room temperature with the mixture of carbon monoxide and ethylene. The autoclave was then heated to the working temperature while stirring. At this temperature the pressure in the autoclave was adjusted at 40 atm and maintained constant using the pressure regulator connected to the gas reservoir. The gas consumption was measured by monitoring the pressure drop of the reservoir. After 1 h, the autoclave was cooled to room temperature and vented.

Products were characterized by GC analysis on a HP 5890 series II apparatus equipped with a 30 m × 0.53 mm × 0.1 μm HP 5 column. The gas phase products (CO/C₂H₄/C₂H₆ molar ratio) were analyzed by GC using a 18 ft × 1/8 SS Silica Gel, 60/80 packed column.

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