Highly active [Pd(AcO)$_2$(dppp)] catalyst for the CO-C$_2$H$_4$ copolymerization in H$_2$O-CH$_3$COOH solvent [dppp = 1,3-bis(diphenylphosphino)propane]

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Dedicated to Professor Renato Ugo on the occasion of his 65th birthday

Abstract

In MeOH, [Pd(AcO)$_2$(dppp)] becomes an efficient catalyst for the perfectly alternated CO-C$_2$H$_4$ copolymerization when used in combination of a relatively large amount of CH$_3$COOH (CH$_3$COOH/Pd, ca. 2.0×10^4). Under 4.56 MPa (CO/C$_2$H$_4$ = 1/1), at 90 °C, 7.5 kg polyketone/g Pd*h are obtained. A significantly higher productivity is obtained in H$_2$O-CH$_3$COOH, in place of MeOH (27.5 kg polymer/g Pd*h under 4.56 MPa (CO/C$_2$H$_4$ = 1/1), 90 °C, H$_2$O = 37% (mol/mol)). Under these conditions the catalyst undergoes only a minor deactivation with time as after 3 h the productivity decreases only by ca. 10%.

The ^{13}C NMR analysis shows that [Pd(AcO)$_2$(dppp)] in CH$_3$COOH-H$_2$O yields a perfectly alternated polyketone of ca. 8000 g/mol bearing only ketonic end groups. During the course of the copolymerization reaction CO$_2$ forms in significant amount. These findings suggest that the insertion of C$_2$H$_4$ into Pd–H bond starts the catalytic cycle, and that alternating insertions of the monomers followed by protonolysis of a Pd–C bond of a Pd-CH$_2$-CH$_2$-(CO-C$_2$H$_4$)$_n$-H growing chain yields the polymer with only keto ending groups and a Pd-OH species; a reaction closely related to the WGS reproduces the starting Pd-hydride; deprotonation of this species to inactive Pd(0) is prevented by the acid.
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Keywords: Palladium catalyst; dppp; Acetic acid; Water; Carbon monoxide; Ethylene; Copolymerization; Polyketones

1. Introduction

The increasing interest for alternating copolymers of CO and olefins is due to the fact that they are at the basis of a new class of melt-processable thermoplastic with interesting physical–mechanical properties, biodegradability, impermeability towards gases and organic solvents and that they can be prepared in high yield using Pd(II) catalysts from cheap and easily available monomers. The discovery of high productivity Pd(II) catalysts made possible the commercialization of these polyketones by Shell and BP Companies [1,2].

The basic principles of the activity of these catalysts have been recently reviewed [3–6]. The metal centre has to be coordinated by a bidentate phosphorus-, nitrogen-ligand, of the type bipy, phen and their alkyl-substituted derivatives, or by ligands containing

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both phosphorus and nitrogen coordinating atoms. Diphosphines with a hydrocarbon backbone of three methylene groups give the most active catalysts, provided that the cationic charge of the metal centre is balanced by a weakly coordinating anion, conjugated base of a strong acid, for example TsOH (*p*-toluenesulfonic acid), HBF$_4$, HPF$_6$, CF$_3$COOH, CF$_3$SO$_3$H [7,8]. *cis*-Coordination of the bidentate ligand assures the chain growth of the polymer, which occurs via alternated insertion of the monomers for thermodynamic and kinetic reasons [3,4,9]. As far as the anion is concerned, the high activity of these systems is thought to be mainly due to the easier access of the monomers to the coordination sites when the anion is weakly coordinated. The catalyst can be prepared in situ from Pd(OAc)$_2$, the ligand and the strong protic acid which, by displacing the coordinating anion AcO creates a facile access of the monomers to Pd(II). Thus the three catalysts Pd(dppp)X$_2$ (X = TsO, CF$_3$COO or CH$_3$COO) prepared in situ by adding dppp and HX to Pd(OAc)$_2$ in MeOH, at 90 °C and 4.56 MPa of total pressure of CO and ethylene (1/1), show a drastically different productivity (6200 g polymer/g of Pd per hour when X = TsO or CF$_3$COO, while no polymer forms when X = CH$_3$COO: Table 1, entries 1 and 5) [7]. The catalyst activity depends also on the Pd/acid ratio and also on the presence of water, which acts as a Pd-H source, one of the species that start the catalytic cycle

[10]. In addition, the catalyst requires the co-presence of an oxidant, such as 1,4-benzoquinone [7], which regenerates the low-valent Pd(I) or Pd(0) species which form because of the reducing conditions of the copolymerization reaction [11].

The CO-C$_2$H$_4$ copolymerization has been accomplished also by using [Pd(OAc)$_2$(dppp)] or [PdCl(CO*t*Bu)(dppp)] as catalyst precursors in combination with alumoxanes, which have the function to abstract the acetate or the chloride ligands, thus activating the metal centre for easy coordination of the co-monomers [12].

In addition, it has been found that the activity increases significantly (ca. 30–40%) when the two methyl groups are introduced in both 1-positions of the dppp ligand [11]. Even better results, as both productivity and catalyst stability are concerned, have been obtained by introducing a methoxy substituent in the *ortho*-position of each phenyl group [13].

The activity of water-soluble Pd(II) catalysts based on the hydrophile bidentate phosphines is also significantly influenced by the nature of the anion [14–20]. Thus, for example employing the catalyst formed in situ from [PdX$_2$L$_n$], dppp-s (dppp-s = 1,3-C$_3$H$_6$(P(C$_6$H$_4$-*m*-SO$_3$Na)$_2$)$_2$, the *meta*-sulphonated analogous of dppp) and an acid, under conditions close to the ones above reported, but in water as solvent and with an excess of acid (acid/Pd = 500/1), the productivity is ca. 4000 or 2250 g

Table 1
Effect of addition of acid on the productivity

Entry	Catalyst system	Molar ratio	Solvent	P_{tot} (MPa)	Productivity (g polymer/g Pd*h)	Reference
1	Pd(OAc)$_2$/dppp/TsOH	1/1/2	MeOH	4.05	6200	[7]
2	Pd(OAc)$_2$/dppp/TsOH	1/1/10	MeOH	4.56	8000	[10]
3	Pd(OAc)$_2$/dppp/TsOH	1/2/10	MeOH	4.56	2550	[10]
4	Pd(OAc)$_2$/dppp/HCOOH	1/1/3000	MeOH	4.56	7500	[21]
5	Pd(OAc)$_2$/dppp/CH$_3$COOH	1/1/100	MeOH	4.05	–	[7]
6	[Pd(TsO)$_2$(NCMe)$_2$]/dppp-s/TfOH	1/1/500	H$_2$O	4.05	3870	[16]
7	Pd(OAc)$_2$/dppp-s/CH$_3$COOH	1/1/500	H$_2$O	4.05	2250	[16]
8	[Pd(CH$_3$)(D-*o*-APPr-S)(NCMe)](TfO)	–	H$_2$O	6.08	32200	[20]
9	[Pd(OAc)$_2$dppp]/CH$_3$COOH	1/20000	MeOH	4.56	7400	[*]
10	[Pd(OAc)$_2$dppp]	–	H$_2$O-CH$_3$COOH	2.53	9450	[*]
11	[Pd(OAc)$_2$dppp]	–	H$_2$O-CH$_3$COOH	4.56	27500	[*]
12	[Pd(OAc)$_2$dppp]/dppp	1/1	H$_2$O-CH$_3$COOH	4.56	14500	[*]
13	[Pd(OAc)$_2$dppp]	–	H$_2$O-CH$_3$COOH	6.08	40000	[*]

Run conditions: [Pd], V_{tot}, H$_2$O: see references; CO/C$_2$H$_4$ = 1/1; T = 90 °C; [*]: present work; dppp = 1,3-C$_3$H$_6$[P(C$_6$H$_5$)$_2$]$_2$; dppp-s = 1,3-C$_3$H$_6$[P(C$_6$H$_4$-*m*-SO$_3$Na)$_2$]$_2$; D-*o*-APPr-S = 1,3-C$_3$H$_6$[P(C$_6$H$_3$-2-OMe-5-SO$_3$Na)$_2$]$_2$; TfO = CF$_3$COO.

polymer/g Pd*h, when the acid is CF_3COOH (X = TsO, L_n = $(MeCN)_2$) or CH_3COOH (X = AcO, n = 0), respectively (Table 1, entries 6 and 7) [16]. Very interesting results were obtained by introducing a methoxy substituent in the *ortho*-position of each phenyl ring of dppp-s: the resulting catalyst is air stable, highly active (25–32 kg polymer/g Pd*h at 90 °C, 6.08 MPa of C_2H_4/CO = 1/1) at very low catalyst concentration [Pd] ca. 10^{-5} mol/l (see Table 1 entry 8) and high molecular weight copolymers are obtained (20–125 kg/mol) [20].

Recently, it has been shown that formic acid, though having a relatively high pK_a (3.75), can be efficiently employed in place of a strong acid of a weakly coordinating conjugated base. Thus the precursor $Pd(AcO)_2$/dppp in combination with HCOOH (HCOOH/Pd = 3000/1), in MeOH as solvent, gives ca. 7500 g polymer/g Pd*h under 4.56 MPa (CO/C_2H_4 = 1/1) at 90 °C (Table 1, entry 4) [21], close to the one obtained when the precursor is employed in combination with TsOH (ca. 8000 g polymer/g Pd*h, TsOH/Pd = 10/1, H_2O = 1000 ppm; see Table 1, entry 2) [10]. Formic acid can act as a Pd-H source as well as the water generated by the esterification of the acid with the solvent.

Here, we present the results of a highly active $Pd(AcO)_2$(dppp)-CH_3COOH catalyst, in MeOH or in CH_3COOH-H_2O as solvents.

2. Experimental

2.1. Reagents

Acetic acid (glacial), methanol (purity >99.5%, 0.01% of water) were purchased from Baker. Palladium(II) acetate, and 1,3-bis(diphenylphosphine)propane, 1,1,1,3,3,3-hexafluoroisopropanol (99%) and $CDCl_3$ were Aldrich products. The complex [Pd-$(OAc)_2$(dppp)] was prepared as reported in [22]. Carbon monoxide and ethylene were supplied by SIAD Company ('research grade', purity >99.9%).

2.2. Equipment

The catalyst components were weighted on a Sartorious Micro balance (precision 0.001 mg). Gas-chromatographic analysis of the gas phase was performed on a Hewlett-Packard Model 5890, Series II chromatograph fitted with a 18 ft × 1/8 SS Silica Gel, 60/80 packed column.

The ^{13}C NMR spectra were recorded on a Bruker Avance 300 spectrometer in 1,1,1,3,3,3-hexafluoroisopropanol/$CDCl_3$ (10/1) using the inverse ^{1}H-Gated Decoupling Technique.

2.3. Carbon monoxide-ethylene copolymerization

The copolymerization reactions were carried out by using a Hastelloy C autoclave of ca. 250 ml provided with a four-blade self-aspirating turbine. Solvent and catalyst were added in a ca. 150 ml Pyrex bottle placed inside the autoclave, in order to prevent contamination by metallic species because of corrosion of the internal surface of the autoclave.

In a typical experiment, 1.100 mg of [Pd($AcO)_2$ (dppp)] (1.73×10^{-3} mmol) was dissolved into 80 ml of H_2O-CH_3COOH (H_2O = 37% (mol/mol)). The autoclave was pressurized at room temperature by ca. 5 atm of the two gases supplied as a 1/1 mixture from a tank reservoir. The autoclave was then heated to 90 °C during ca. 10 min. The pressure was then adjusted to the desired value (typically 4.56 MPa total pressure) and maintained constant throughout the experiment (1 h, rate stirring 11.7 Hz) by continuously supplying the gases from the reservoir. At the end of the experiment the autoclave was quickly cooled and carefully depressurized. The slurry product was filtered, washed with water and acetone and dried under vacuum at 80 °C.

2.4. Solubility measurements

The solubility of the monomers in the solvent of reaction was measured by an absorption technique. In a typical experiment a known volume of solvent (V_s = 80 ml) was charged into the autoclave used for the copolymerization reaction and heated to a desired temperature (90 °C). After the thermal equilibrium was attained, the void space above the liquid was carefully washed (without stirring the solvent) with a monomer and pressurized to a desired value (P_A) by supplying the monomer from a tank reservoir of 88.0 ml volume (V_r) maintained at constant temperature (T). The initial pressure in the reservoir (P_i) was adjusted at P_i > P_A. The liquid in the autoclave was then vigorously

stirred till the pressure of the reservoir dropped to a constant final value, P_f. The moles of A absorbed are $n_{A,abs} = V_r(P_i - P_f)(zRT)^{-1}$ and the molar fraction of A in the solvent is $X_A = n_{A,abs}(n_{A,abs} + n_{solvent})^{-1}$.

The Henry's law constant H (atm) has been calculated as $H = P_A X_A^{-1}$ for $P_A \to 0$.

3. Results and discussion

3.1. Effect of the reaction conditions on the catalyst activity

Under the conditions reported in Fig. 1, [Pd(AcO)$_2$ (dppp)] gives rise to an efficient catalyst even in combination with a weak acid of a coordinating conjugated base such as CH_3COOH ($pK_a = 4.75$), provided that the acid is employed in a relatively large excess ($CH_3COOH/Pd > 2.0 \times 10^4$). Thus it is evident that, under these conditions, the ac-

etate anion does not prevent the coordination of the monomers. This is a rather surprising result since the Pd(AcO)$_2$/dppp/AcOH (1/1/100) system in MeOH is inactive under the same conditions [7]. For comparative purposes, in Fig. 1 is also reported the effect of the addition of HCOOH or TsOH on the activity of [Pd(AcO)$_2$(dppp)].

When the acid is not used in large excess the catalyst decomposes to inactive Pd(0) complexes or to colloidal palladium. The decomposition takes place in the presence of water, probably via formation of a Pd-H species, which however decomposes before reacting with C_2H_4, and then with nCO and nC$_2$H$_4$ to give the polymer. In the presence of a large excess of the acid the last equilibrium of reactions (1) is shifted toward the hydride that starts the catalytic cycle (see also the discussion of the proposed catalytic cycle):
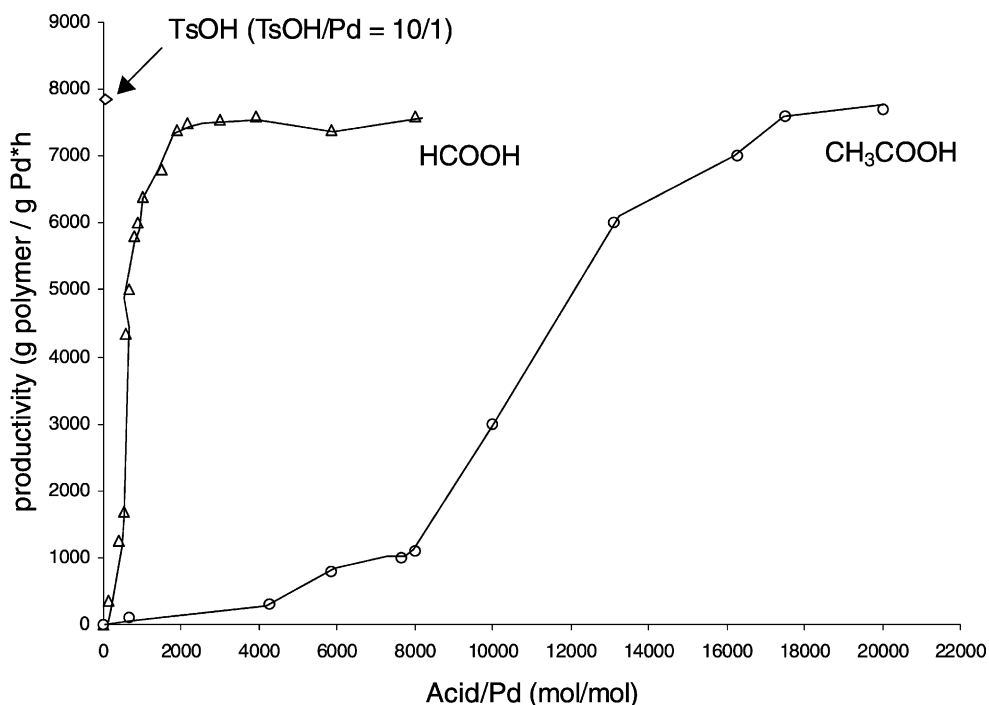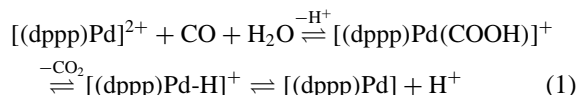
$$[(dppp)Pd]^{2+} + CO + H_2O \overset{-H^+}{\rightleftharpoons} [(dppp)Pd(COOH)]^+$$
$$\overset{-CO_2}{\rightleftharpoons} [(dppp)Pd\text{-}H]^+ \rightleftharpoons [(dppp)Pd] + H^+ \quad (1)$$

Fig. 1. Effect of addition of acids on the productivity. Run conditions: [Pd(OAc)$_2$dppp] $= 8.5 \times 10^{-3}$ mmol; $P_{tot} = 4.56$ MPa (CO/C$_2$H$_4 = 1/1$, at the working temperature); $T = 90\,°C$; $V_{tot} = 80$ ml (MeOH + acid); H$_2$O $= 100$ ppm (initially present in the solvent); reaction time $= 1$ h; stirrer speed $= 11.7$ Hz.

Formation of the cationic hydride $(PdL_3H)^+(TFA)^-$ was observed by NMR when $Pd(PPh_3)_4$ was allowed to react with a 70% aqueous solution of HTFA at $-25\,^\circ C$ [23,24] or when a solution of $Pd(OAc)_2$ and tppts (tppts $= P(C_6H_4\text{-}m\text{-}SO_3Na)_3)$ in a 60% (v/v) aqueous trifluoroacetic acid (HTFA). The formation of the hydride occurs via reduction of Pd(II) to Pd(0) by H_2O-CO followed by oxidation of Pd(0) with a proton [25].

As in the case when HCOOH is employed in MeOH, the esterification of CH_3COOH yields water, which acts also as a hydride source. In order to separate the effect of the acid from that of the water we carried out some experiments in pure CH_3COOH as solvent in the absence of H_2O. The system is quite inactive, although it does not decompose to palladium metal. The catalytic activity strongly depends on the presence of H_2O (Fig. 2) and passes through a maximum (ca. 27500 g polymer/g Pd*h) when $X_{H_2O} = 37\%$. This is a remarkable result as the productivity is 4.4 times higher than in MeOH (see Table 1, entries 1 and 11) even though the solubility of the monomers in H_2O-CH_3COOH is significantly

lower as deduced by comparing the solubility of the monomers ($H_{CO,MeOH} = 273.58\,MPa$, $H_{C_2H_4,MeOH} = 51.68\,MPa$, $H_{CO,37\%\ H_2O\text{-}CH_3COOH} = 1165.24\,MPa$, $H_{C_2H_4,37\%\ H_2O\text{-}CH_3COOH} = 149.96\,MPa$). The productivity remains appreciable also when water is in large excess. For example, for $X_{H_2O} = 55\%$ the catalytic activity is close to that of the $Pd(AcO)_2$/dppp/ TsOH system in MeOH [10] even though the solubility of CO and C_2H_4 in H_2O-CH_3COOH is 7.1 and 5.5 times lower than in MeOH ($H_{CO,55\%\ H_2O\text{-}CH_3COOH} = 1955.57\,MPa$, $H_{C_2H_4,55\%\ H_2O\text{-}CH_3COOH} = 288.78\,MPa$). Since the solubility of the monomers decreases on increasing the concentration of H_2O in the solvent, the fact that the activity passes through a maximum must be due to a combined promoting effect of H_2O and the acid. Notice also that the maximum occurs at the same concentration of H_2O irrespective of the catalyst concentration.

Under the conditions reported in Fig. 2 the copolymerization rate is not limited by the rate of mass transfer of the monomers at the gas/liquid interphase as the amount of polymer formed under the conditions reported in Fig. 3 increases linearly with increasing
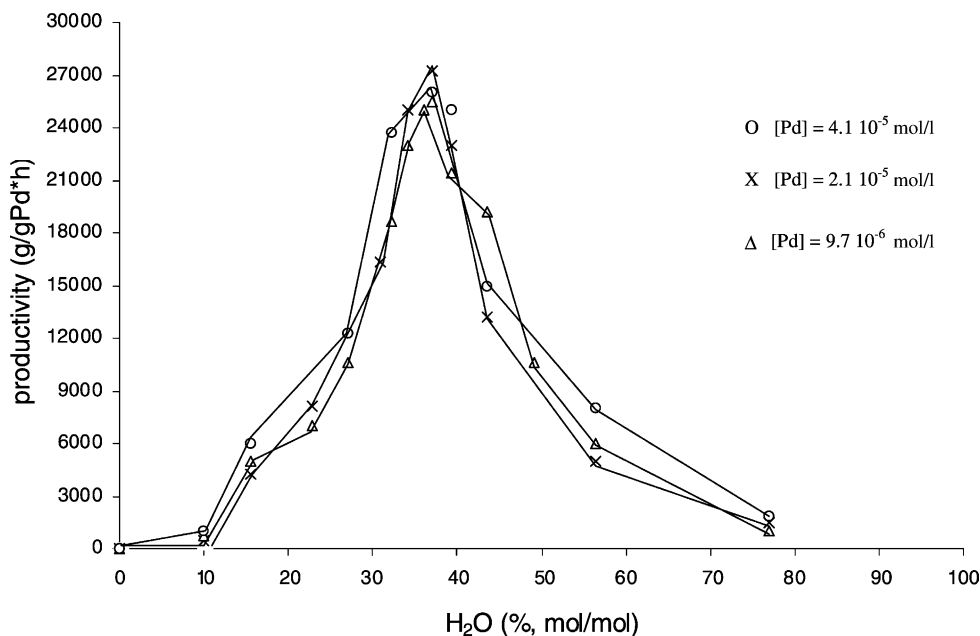

Fig. 2. Effect of H_2O on the productivity at different concentrations of catalyst precursor. Run conditions: catalyst precursor $= [Pd(AcO)_2$ (dppp)], $P_{tot} = 4.56\,MPa$ (CO/$C_2H_4 = 1/1$, at the working temperature); $T = 90\,^\circ C$; $V_{tot} = 80\,ml$; solvent $= H_2O + CH_3COOH$; reaction time $= 1\,h$; stirrer speed $= 11.7\,Hz$.
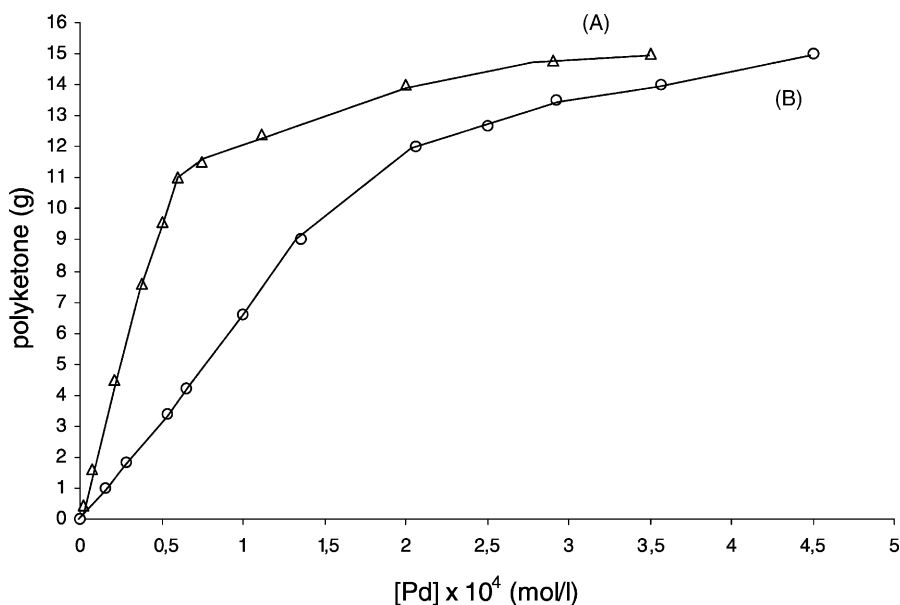
Fig. 3. Catalytic activity as a function of catalyst concentration. Run conditions: curve A: catalyst precursor = [Pd(AcO)$_2$(dppp)], P_{tot} = 4.56 MPa (CO/C$_2$H$_4$ = 1/1, at the working temperature); T = 90 °C; V_{tot} = 80 ml (H$_2$O + CH$_3$COOH; H$_2$O = 37% (mol/mol)); reaction time = 1 h; stirrer speed = 11.7 Hz; curve B: catalyst system = Pd(OAc)$_2$/dppp/HCOOH = 1/1/3000, H$_2$O (initially present in the solvent) = 500 ppm, V_{tot} = 80 ml, solvent = MeOH; P_{tot} = 4.56 MPa (CO/C$_2$H$_4$ = 1/1, at the working temperature), T = 90 °C, reaction time = 1 h, stirrer speed = 11.7 Hz.

catalyst concentration up to 6×10^{-5} mol/l (curve A), which is above the highest concentration reported in Fig. 2. At concentrations higher than 6×10^{-5} mol/l the increase of the reaction rate is less pronounced and tends to a plateau, suggesting that the reaction is limited by the rate of mass transfer. The amount of polymer formed using the catalyst [Pd(AcO)$_2$(dppp)] in CH$_3$COOH-H$_2$O is compared with that obtained with the system Pd(AcO)$_2$/dppp/HCOOH in MeOH (curve B) [21]. At relatively high catalyst concentration the reaction rates reach the same plateau (ca. 1.5×10^4 g polymer/h) because they are limited by the same rate of mass transfer of the monomers. Notice that, in order to reach the plateau it is necessary to use the latter catalyst in higher concentration because it is less active.

Further support that, in the range of catalyst concentration reported in Fig. 2, the reaction is not limited by the mass transfer comes from experiments carried out at different temperatures. Fig. 4 shows the effect of the temperature on the productivity of the catalyst. The apparent activation energy of 14 kcal/mol evaluated by the Arrhenius plot (supposing that the

solubility of the monomers does not change appreciably with the temperature) confirms that the reaction rate is not limited by the mass transfer [21,26,27].

The productivity increases with the total pressure, reaching 40 kg polymer/g Pd*h at 6.08 MPa (see Table 1, entries 10, 11, 13).

Fig. 5 shows that the catalyst undergoes just a minor deactivation with time as after 3 h the productivity decreases only by about 10% of the initial value. For the water-soluble catalyst [Pd(CF$_3$COO)$_2$(Na$_2$dppp-s)] 2THF/TsOH (TsOH/Pd = 20–300) it has been reported that after 3 h the catalytic activity, measured by plotting the consumption of the gaseous monomers versus time for 3 h reactions, is reduced to about 1/10 of the maximum value that is reached after ca. 30 s, even in the presence of benzoquinone (BQ/Pd = 80) [17]. The fact in the present case the activity remain almost constant after 3 h suggests that CH$_3$COOH efficient by reoxidizes Pd(0) with formation of a Pd-H species which starts the catalytic cycle (see the proposed catalytic cycle of Scheme 1, equilibrium **a**).

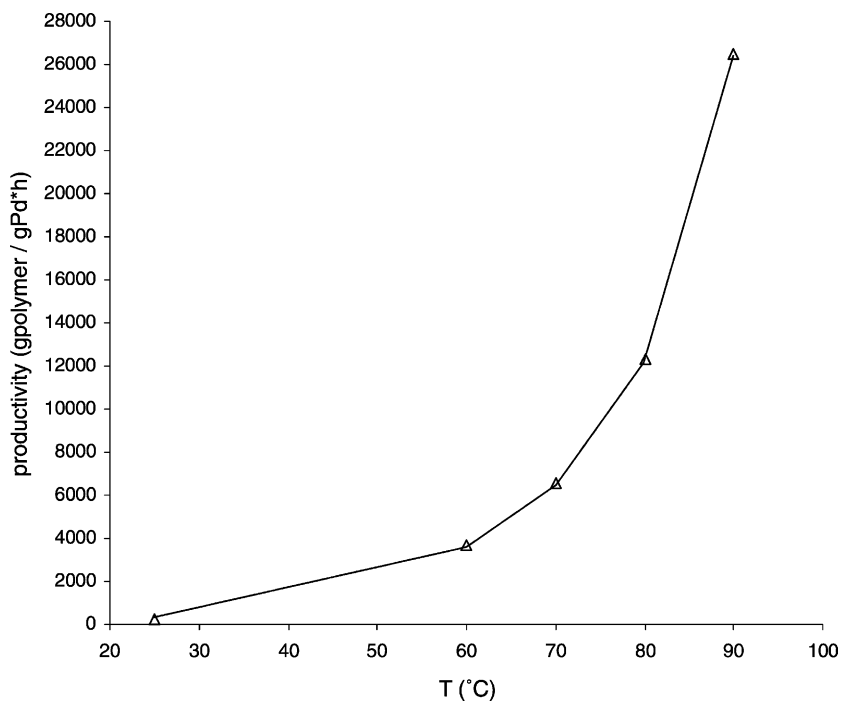Unlike the water-soluble catalytic system just mentioned, which yields a higher productivity when 2 eq.

Fig. 4. Effect of temperature on the productivity. Run conditions: $[Pd(AcO)_2(dppp)]$ = 1.103 mg (0.00169 mmol), P_{tot} = 4.56 MPa (CO/C_2H_4 = 1/1, at the working temperature); V_{tot} = 80 ml (H_2O + CH_3COOH; H_2O = 37% (mol/mol)); reaction time = 1 h; stirrer speed = 11.7 Hz.
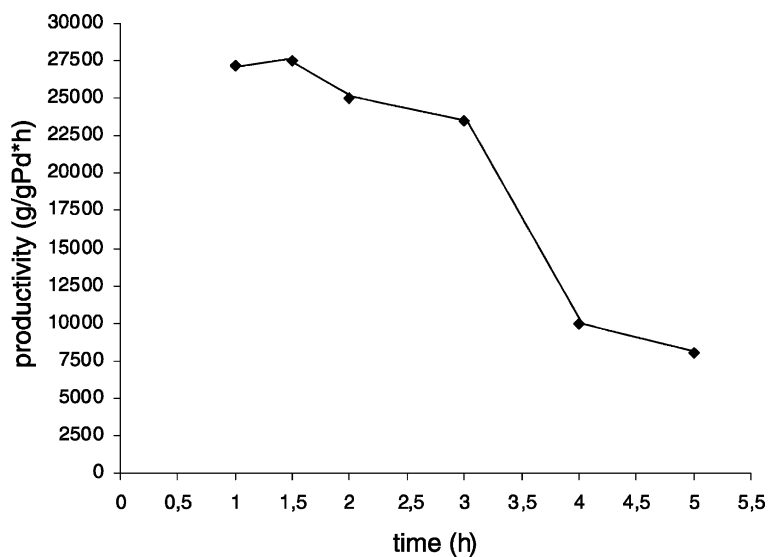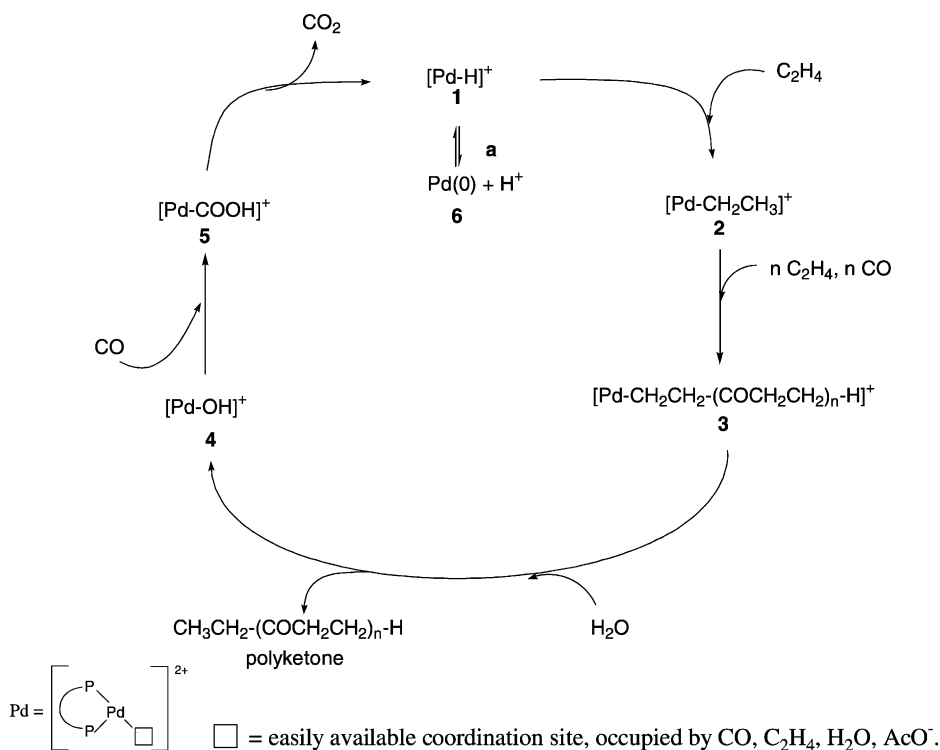

Fig. 5. Effect of reaction time on the productivity. Run conditions: $[Pd(AcO)_2(dppp)]$ = 1.103 mg (0.00169 mmol), P_{tot} = 4.56 MPa (CO/C_2H_4 = 1/1, at the working temperature); T = 90 °C; V_{tot} = 80 ml (H_2O + CH_3COOH; H_2O = 37% (mol/mol)); stirrer speed = 11.7 Hz.

Scheme 1. Proposed catalytic cycle for the CO-C_2H_4 copolymerization.

of free ligand are added (6.8 kg polyketone/g Pd*h compared to 4.8 kg polyketone/g Pd*h [17]), the addition of dppp to [Pd(AcO)$_2$(dppp)] has a detrimental effect (Table 1, entries 11 and 12), as found for the system Pd(AcO)$_2$/dppp/TsOH in MeOH (Table 1, entries 1 and 2) [10]. The decrease in productivity suggests that [Pd(dppp)]$^{2+}$ is (partially) converted to less active [Pd(dppp)$_2$]$^{2+}$ [28].

3.2. On the proposed catalytic cycle

The ^{13}C NMR analysis shows that the [Pd(AcO$_2$)$_2$(dppp)] complex in CH_3COOH-H_2O yields a perfectly alternated polyketone of ca. 8000 g/mol bearing exclusively ketonic end groups. GC analysis of the gas mixture during the course of the copolymerization reaction reveals the presence of significant amounts of CO_2. On the basis of these findings we suggest that the Pd(II) precursor is at equilibrium with several species in which water may replace one or both acetate anions and that coordinated water may dissociate a proton with formation of a Pd-OH species, which

inserts CO to give a Pd-COOH complex which, upon decarboxylation, yields the Pd-hydride (1). Species (1) starts the catalytic cycle by inserting a molecule of C_2H_4 (species 2); the chain grow occurs via perfectly alternating insertion of CO into a Pd–alkyl bond and of C_2H_4 into a Pd–acyl bond; termination occurs only by protonolysis (in Scheme 1 exemplified by H_2O) of a Pd–alkyl bond (3) with reformation of a Pd-OH species (4), which re-enters the catalytic cycle by interacting with CO and yielding a Pd-COOH species (5) and then a Pd-H species (1) as just proposed. Excess of acid inhibits the hydrolysis of a Pd–acyl bond as observed in water with sulphonated dppp ligands [15,20]. The overall mechanism is basically similar to the one proposed by Bianchini et al. with water-soluble Pd(II) catalysts [17] (species 3 can be actually a β-chelate at equilibrium with an enolate isomer which undergoes protonation of the C2 carbon atom [29]). The CH_3COOH-H_2O reaction medium not only guarantees a sufficient solubility of the two monomers and the catalytic system but, more important, on one hand the acid stabilizes the [Pd-H]$^+$ species (equilibrium **a**

of Scheme 1; see also the last equilibrium of reactions 1), on the other it is likely that water prevents coordination of AcO to the cationic hydride (**1**) and hence its deprotonation via reductive elimination of AcOH. It is interesting to point out that $[PdH(dppp)]^+$ is not stable in MeOH and slowly deprotonates with formation of the Pd(0) complex [Pd(dppp)]. The latter may separate Pd metal and free ligand, which in turn may react with $[Pd(dppp)]^{2+}$ to give a catalytically less active bis-chelate complex $[Pd(dppp)_2]^{2+}$ [28]. Moreover, the acid may prevent the Pd-OH species (**4**) from forming a less active μ-OH binuclear complex [28].

In the Scheme 1, Pd(II) is four or five-coordinated, two sites being occupied by the bidentate ligand, another site by the growing polymer, the fourth or fifth coordination sites by the monomers or by water or the acetate anion. A kinetic study employing preformed $[Pd(TsO)(H_2O)(dppp)](TsO)$ in MeOH showed that the experimental data fit equally well a so-called "one- or two-sites" model, having Pd(II) four- or five-coordinated by the monomers, respectively [26,27]. In the present case, water or the acetate anion can compete for coordination of the monomers, but do not prevent it. Notice that also on introducing a methoxy substituent in the *ortho*-positions of each phenyl rings of dppp-s the resulting catalyst is very active, even though the oxygen atom of the methoxy group can compete for coordination with the monomers [20]. The coordination of *ortho*-methoxy substituents was observed in the solid state in $[Pd(P(C_6H_2-2,4,6-(OMe)_3)_3)_2](BF_4)_2$ [30]. Also the Pd(II) cationic complexes with potentially hexadentate diphosphine ligands $(ROCH_2CH_2)_2P(CH_2)_3P(CH_2CH_2OR)_2$ [31] or cationic $[(C-D)Pd(P-P)]^+$ [32] have been successfully employed in the CO-C_2H_4 copolymerization. In the first case the ether–oxygen donor forms only a weak Pd–O interaction so that the monomers have facile access to the metal centre [31]. In the latter case the bidentate C–D ligand (D = NR$_2$, P(*o*-Tol)$_2$) is coordinated to the metal by a Pd–C σ bond and a Pd–N or Pd–P labile bond which does not prevent coordination of the monomers [32].

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