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Carbon monoxide–ethylene copolymerization catalyzed by a $Pd(AcO)_2$/dppp/TsOH [1] system: the promoting effect of water and of the acid

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Abstract

For the title copolymerization the catalyst productivity (g-polymer/g-Pd · h) is significantly influenced by the presence of water and of the acid as it passes through a maximum upon increasing concentration of H_2O and of TsOH. In the presence of 450 ppm of H_2O, the maximum productivity is ca. 3.7 times higher than when the copolymerization is carried out in the presence of 1% of trimethylorthoformate, used as H_2O scavenger in MeOH as solvent, at 90°C, under 45 atm of total pressure, employing the catalyst precursor in the molar ratio Pd/dppp/TsOH 1/1/2 ([Pd] 5.6×10^{-5} mol · l^{-1}). Under similar conditions, but under 60 atm of the two monomers, in the presence of 900 ppm of H_2O and when employing an excess of the acid (TsOH/Pd 6.4) the productivity reaches a maximum of ca. 11500 g-polymer/g-Pd · h, which is 1.4 times higher than that obtained when the TsOH/Pd ratio is 2/1.

The promoting effect of H_2O is ascribed to the possibility that a higher concentration of active Pd–H species, which are proposed to initiate the catalytic process through the insertion of the olefin into a Pd–H bond, is achieved through the interaction of carbon monoxide with water on the metal center, via a reaction closely related to the water gas shift reaction.

It is also proposed that the promoting effect of the acid is due to the reactivation of inactive Pd(0) species, which inevitably form under the reducing reaction conditions, with formation of active Pd–H species.

When the copolymerization is carried out in the presence of benzoquinone (BQ), either under the reaction conditions in which the productivity reaches a maximum or under unfavorable conditions, that is, in the presence of low or relatively high concentrations of water, the productivity has an average value of ca. 7000 g-polymer/g-Pd · h. Since it was found by other research groups that in the presence of BQ the polymer takes origin mainly through the insertion of CO into a Pd–OCH_3 species whose formation is favored in the presence of BQ, the findings presented above give further support to the suggestion that the promoting effect of H_2O and of TsOH are due to the possibility that, when present in appropriate amounts, they favour the formation of Pd–H species which start the catalytic cycle.

Keywords: Copolymerization; CO; Ethylene; Polyketones; Cationic complexes; Palladium

1. Introduction

Palladium complexes of the type $Pd(L–L)X_2$ (L–L = monodentate or bidentate phosphorus or nitrogen ligands; X = weakly coordinating an-

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[1] dppp = 1,3-bis(diphenylphosphino)propane; TsOH = *p*-toluenesulfonic acid.

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ion) have been found to be highly efficient catalysts in the strictly alternating copolymerization of olefins with carbon monoxide to polyketones [1–16]. For ethylene–carbon monoxide copolymerization particularly active are those systems where L–L is a bidentate ligand of general formula $PPh_2(CH_2)_nPPh_2$, with $n = 2$–5 and X = TsO, BF_4, CF_3COO, CF_3SO_3. The maximum copolymerization rate was observed with $n = 3$. A sound explanation of why the catalyst is so efficient in promoting the chain growth through the alternate insertion of the olefin and carbon monoxide was given by several research groups [5,17,18]. The resulting material is a mixture of polyketones which differ not only for the chain length, but also for the nature of the terminal groups, depending on the initiation and termination steps. The most abundant polymer (indicated as polymer I) presents ethyl and ester end groups ($-COOCH_3$, when the copolymerization is carried out in methanol). The other two couples of end groups are ester–ester (polymer II) and ethyl–ethyl (polymer III). It has been proposed that polymer I takes origin from the initial insertion of CO into a $[Pd(OCH_3)]^+$ bond, followed by sequential insertion of ethylene and CO in the chain growth process, which ends by protonolysis by MeOH which regenerates the starting catalytic species [5]. Alternatively, polymer I can take origin from the initial insertion of the olefin into a $[Pd-H]^+$ bond, followed by the chain growth process, which ends by methanolysis giving the ester end group with regeneration of the starting hydride. Polymer II forms when, after the initial step of the insertion of CO into a $[Pd-(OCH_3)]^+$ bond, the chain growth is ended by nucleophilic attack of MeOH on a $[Pd-(acyl)]^+$ bond. Polymer III forms when it begins from the initial insertion of the olefin into a $[Pd-H]^+$ bond and the chain growth is ended by protonolysis of a $[Pd-(alkyl)]^+$ bond. It should be observed that the last two mechanisms are strictly connected to keep the charge balance and to maintain the catalytic activity. In any case the polymer takes origin either from a $[Pd-H]^+$ or a $[Pd-(OCH_3)]^+$ species. Thus, in order to improve the productivity of the catalytic system, one has to search for those conditions that allow us to maximize the concentration of active $[Pd-H]^+$ or $[Pd(OCH_3)]^+$ species.

We found that the productivity can be significantly improved by carrying out the copolymerization reaction in the presence of an appropriate amount of H_2O and with a convenient excess of TsOH.

2. Results and discussion

2.1. On the stability of the catalytic system

The copolymerization of ethylene with carbon monoxide, schematized by reaction (1), was carried out in methanol employing the same catalyst precursor used by Drent et al. [5] prepared in situ by adding $Pd(AcO)_2$, dppp and TsOH in the desired ratio.

$$C_2H_4 + nCO \xrightarrow{CH_3OH} R(C_2H_4CO)_nR' \quad (1)$$

$R = C_2H_5CO$, $R' = OCH_3$; $R = CH_3OCO$, $R' = OCH_3$; $R = C_2H_5CO$, $R' = C_2H_5$.

The formation of the catalyst in situ is often accompanied by decomposition to palladium metal to a variable extent. The monomers themselves can act as reducing agents according to reactions (2) and (3):

$$Pd^{2+} + CO + H_2O \rightarrow Pd_{met} + CO_2 + 2H^+ \quad (2)$$

$$Pd^{2+} + C_2H_4 + H_2O \rightarrow Pd_{met} + CH_3CHO + 2H^+ \quad (3)$$

In addition, even the dppp ligand, which plays an important role in stabilizing the Pd^{2+} species, can reduce it through reaction (4):

$$Pd^{2+}dppp + H_2O \rightarrow Pd_{met} + dpppO\,(\text{or}\,dpppO_2) + 2H^+ \quad (4)$$

All three reactions, (2)–(4), lead to an oxidized compound in the presence of H_2O. The ability of carbon monoxide of reducing Pd^{2+} to the metal in the presence of H_2O is well known [19,20]. Reaction (3) is relevant to the well known process for the production of acetaldehyde based on the oxidation of ethylene with oxygen in the presence of a Pd–Cu catalytic system [21,22]. Reaction (4) is related to the oxidation of tertiary phosphines to the corresponding oxide by $Pd(AcO)_2$ [23]. In the present case, the presence of oxides of the bidentate ligand (dpppO or $dpppO_2$) has been proved by ^{31}NMR spectroscopy [24].

Moreover, the same solvent can reduce Pd^{2+} according to reaction (5) [25]. In addition, in the presence of carbon monoxide, formation of dimethylcarbonate can lead to reduced palladium [26,27], as schematized by reaction (6):

$$Pd^{2+} + CH_3OH \rightarrow Pd_{met} + HCHO + H_2 \qquad (5)$$

$$Pd^{2+} + 2CH_3OH + CO \rightarrow Pd_{met} + (CH_3O)_2CO + 2H^+ \qquad (6)$$

Palladium metal is not catalytically active in the copolymerization of carbon monoxide and ethylene, even in the presence of dppp and of TsOH. Attempts were made to dissolve $Pd(AcO)_2$ in methanol saturated with the two monomers in the absence of dppp and of TsOH. Formation of Pd_{met} was noticed after a short time. After some minutes the diphosphine and the acid were added. No catalytic activity was observed at 90°C under 40–60 atm of the two monomers. It is interesting to mention that the carbonylation of ethylene catalyzed by a Pd/C system in the presence of hydrochloric acid dissolved in ethanol yields the propionate ester as main product, together with 4-oxohexanoate, a γ-ketoester which can be considered an oligomer made of one carbon monoxide and one ethylene unit [28].

In the reactions (2)–(6), the reduced palladium can also be a complex of Pd(0), such as, Pd(dppp)L (L dppp, CO, etc.).

As a consequence of the reduction of Pd^{2+}, not only is the concentration of the catalyst lower than expected, but the system also becomes unbalanced towards an excess of diphosphine which depresses the catalytic activity as shown in Fig. 1.

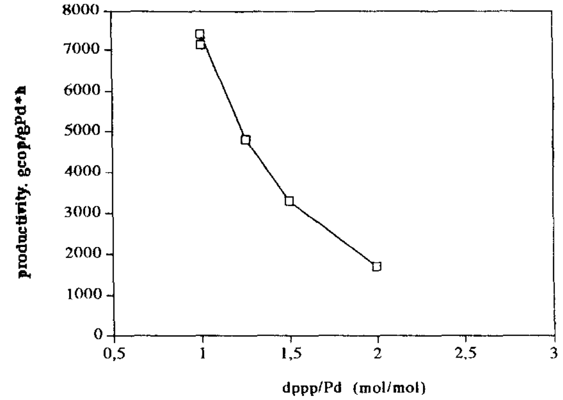

Fig. 1. Influence of the dppp/Pd ratio on the productivity. Run conditions: pressure: 45 atm; temperature: 90°C; MeOH: 50 ml; [Pd]: 5.6×10^{-5} mol·l^{-1}, 0.63 mg of $Pd(AcO)_2$; Pd/TsOH: 1/2 (mol/mol); [H_2O]: 450 ppm (w/w); reaction time: 2 h.

2.1.1. *Influence of the concentration of the catalyst precursor on the productivity*

Preliminary experiments showed that the productivity is significantly influenced by the concentration of the catalyst. Fig. 2 shows that the productivity passes through a maximum with increasing dilution of the precursor. At 90°C, under 45 atm of carbon monoxide and ethylene, the productivity is 6000 g-pol/g-Pd · h when [Pd] = 5.5×10^{-5} mol · l^{-1}, close to the value reported by Drent under similar conditions [5]. Further dilution leads to a lower productivity, probably because the solvent contains some impurity such as Cl^- in an amount comparable to that of the catalyst. It is known that Cl^- coordinates to the metal giving rise to a catalytic system that promotes the hydroesterification of ethylene instead of the copolymerization process [5].

The fact that the productivity decreases with increasing concentration of palladium suggests that in solution there are monomeric catalytic species in equilibrium with dimeric ones and that the latter are less active. Equilibria of this type have been established for related systems. For example, it has been reported that the bisaquo complex (**1**) undergoes equilibrium (7), which is shifted towards monomer (**1**) in an acidic medium [29]:

$$\underset{(1)}{[(\mathrm{dppp})\mathrm{Pd}(\mathrm{H_2O})_2]^{2+}\,2\mathrm{X}^-} \rightleftharpoons \underset{(2)}{[(\mathrm{dppp})\mathrm{Pd}(\mu\text{-}\mathrm{OH})_2\mathrm{Pd}(\mathrm{dppp})]^{2+}}\,2\mathrm{X}^- + 2\mathrm{H}^+ \tag{7}$$

The fact that the productivity increases when the catalytic system based on $Pd(AcO)_2$/dppp/TsOH is used with an appropriate excess of acid (see later) gives further support to the suggestion given above about the lowering of the productivity with increasing concentration of the precursor.

In addition, it was found that the closely related hydride (**3**) (bdpp (2*S*,4*S*)-2,4-bis(diphenylphoshino)pentane) undergoes the following equilibria which lead to the formation of the dinuclear bridging hydride carbonyl complex of Pd(I) (**5**) through reactions (8) and (9) and that the dinuclear complex inserts an olefin such as styrene at a much lower rate than the monomer does [30]. As will be seen below, both the presence of hydrides and the insertion of ethylene into a Pd–H bond are of paramount importance in the carbon monoxide–ethylene copolymerization process.

$$\underset{(3)}{\mathrm{Pd(bdpp)HCl}} + \mathrm{CO} \rightarrow \underset{(4)}{\mathrm{Pd(bdpp)(CO)}} + \mathrm{HCl} \tag{8}$$

$$(3) + (4) \rightarrow [\mathrm{Pd_2}(\mu\text{-}\mathrm{H})(\mu\text{-}\mathrm{CO})(\mathrm{bdpp})_2]^+\mathrm{Cl}^- \tag{9}$$

As illustrated above, the presence of H_2O favours the reduction of Pd^{2+} which occurs together with the formation of oxygenated products and of protons. On the other hand the protons can add to the reduced palladium with formation of hydride species as schematized by equilibrium (10) [31,32]:

$$\mathrm{Pd_{red}} + \mathrm{H}^+ \rightarrow \underset{(6)}{[\mathrm{Pd{-}H}]^+} \tag{10}$$

Moreover, it is also known that reactions (2), (3) and (5) occur via palladium-hydride intermediates. Thus, while H_2O and MeOH may be involved in the reduction of Pd^{2+}, they can be also a source of hydrides, which are believed to play a key role in the catalytic cycle of the

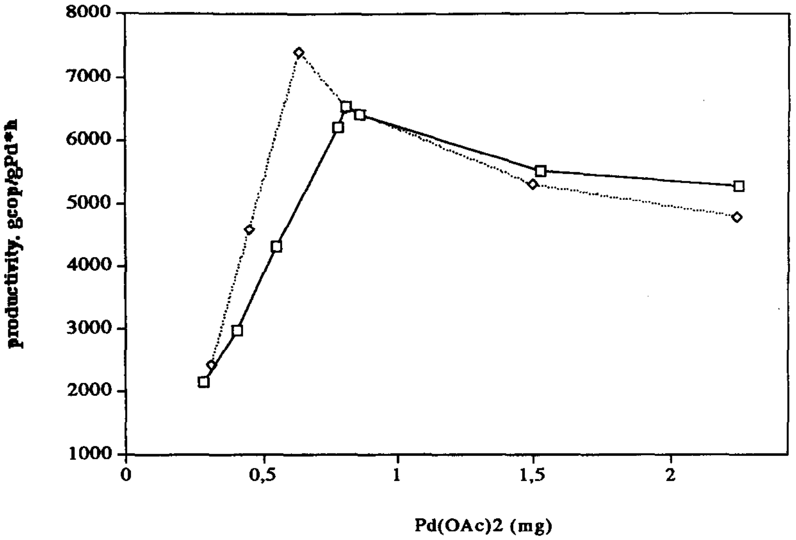

Fig. 2. Influence of the concentration of the catalyst precursor on the productivity. Run conditions: pressure: dotted line 45 atm, solid line 60 atm; temperature: 90°C; MeOH: dotted line 50 ml; solid line 80 ml; Pd/dppp/TsOH: 1/1/2 (mol/mol); $[H_2O]$: dotted line 450 ppm; solid line 400 ppm, (w/w); reaction time: 2 h.

copolymerization process. If the insertion of ethylene into a Pd–H bond is faster than the loss of a proton, schematized by equilibrium (10), then the copolymerization process can start.

2.1.2. Influence of the concentration of water on the productivity

The reaction rate is significantly influenced by the presence of water. Under the conditions reported together with Fig. 3 the productivity increases from 2000–2600 up to 7400–8400 g-pol/g-Pd · h in the presence of 450 or 900 ppm of H_2O in methanol, under 45 or 60 atm, respectively. A further increase of H_2O concentration causes a lowering of the reaction rate. The trend suggests that H_2O competes with the monomers for the coordination to the metal.

That H_2O is capable of coordinating to palladium is well documented [33]. Relevant to this work we found that the reaction of $Pd(AcO)_2$ with dppp gives $Pd(dppp)(AcO)_2$, which, after reaction with TsOH in wet methanol, yields the cationic complex $[Pd(dppp)(H_2O)(TsO)](TsO)$, in which a molecule of H_2O enters the coordination of the metal [24]. It was also found that the closely related complex $Pd(dppp)(OSO_2CF_3)_2$ reacts with one equivalent of H_2O or with two or more equivalents of H_2O to yield the corresponding monoaquo and diaquo cationic complexes $[Pd(dppp)(H_2O)(OSO_2CF_3)](OSO_2CF_3)$ or $[Pd(dppp)(H_2O)_2](OSO_2CF_3)_2$, respectively [34].

The fact that in the presence of an appropriate amount of H_2O the productivity increases may be due to the possibility that H_2O increases the concentration of hydride species through a reaction strictly related to the water gas shift reaction (WGSR) which is schematized below:

$$
\begin{aligned}
&Pd^{2+} + CO \\
&\quad \rightarrow [Pd{-}(CO)]^{2+} + H_2O \\
&\quad \xrightarrow{-H^+} [Pd{-}(COOH)]^+ \\
&\qquad\qquad (\mathbf{6}) \\
&\quad \xrightarrow{-CO_2} [Pd{-}H]^+ \xrightarrow{+H^+} Pd^{2+} + H_2 \qquad (11)
\end{aligned}
$$

The ability of palladium complexes to catalyze the WGSR is well known [32,35,36]. In the presence of ethylene, hydride (**6**) inserts the olefin starting the catalytic cycle that leads to polymer I (or to polymer III). Thus it appears that the insertion of ethylene into a Pd–H bond is faster than the evolution of hydrogen.

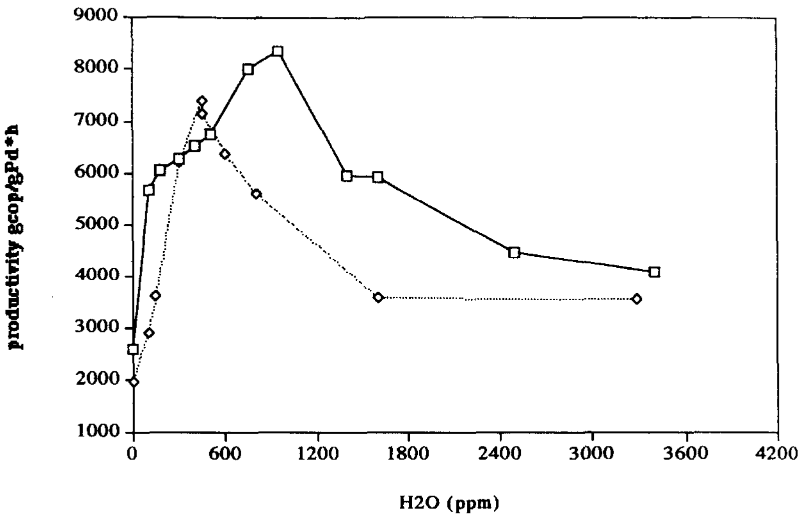

Fig. 3. Influence of the water concentration on the productivity. Run conditions: pressure: dotted line 45 atm, solid line 60 atm; temperature: 90°C; MeOH: dotted line 50 ml; solid line 80 ml; [Pd]: dotted line 5.6×10^{-5} mol · l^{-1}, solid line 4.5×10^{-5} mol · l^{-1}; Pd/dppp/TsOH = 1/1/2 (mol/mol); reaction time: 2 h.

It should be observed that under a higher pressure of ethylene and carbon monoxide the maximum of productivity shifts towards higher values of H_2O concentration. This trend gives further support to the suggestion that H_2O competes with the monomers for coordination to the metal.

The minimum H_2O concentration was accomplished by adding 1% of trimethylorthoformate. The fact that in this case the productivity is significantly lower suggests that the concentration of active $[Pd{-}H]^+$ species is rather low. Under these conditions the catalytic cycle may start from a $[Pd{-}(OCH_3)]^+$ species and/or from a hydride that forms from this species through reaction (12) [18]:

$$[Pd{-}(OCH_3)]^+ \rightarrow [Pd{-}H]^+ + HCHO \qquad (12)$$

A trend similar to that shown in Fig. 3 was found for the synthesis of dialkyl ketones from olefins (ethylene or propylene), carbon monoxide and hydrogen, catalyzed by a $Pd(AcO)_2/PPh_3/CF_3COOH$ system in the presence of H_2O. The same reaction occurs even in the absence of hydrogen. It was proposed that the formation of the ketone occurs via a Pd–H intermediate that forms upon interaction of CO with H_2O, which eventually leads to reduction to a Pd(0) complex. Protonation of the Pd(0) species yields also a palladium hydride complex as schematized by the following equilibria [31,32]:

$$PdL_2X_2 + CO + H_2O \xrightarrow[(a)]{-CO_2,\,-HX,\,L} PdL_nHX \underset{(b)}{\rightleftharpoons} PdL_4 + HX \qquad (13)$$

2.1.3. *Influence of the concentration of TsOH on the productivity*

Fig. 4 shows that the productivity is strongly influenced by an excess of TsOH with respect to stoichiometry of the reaction of displacement of the acetate anion from the starting palladium salt:

$$Pd(AcO)_2 + dppp + 2TsOH \xrightarrow{MeOH} Pd(dppp)(TsO)_2 + 2MeCOOMe + 2H_2O \qquad (14)$$

The highest productivity is obtained when the TsOH/Pd ratio is ca. 7/1. In the presence of a

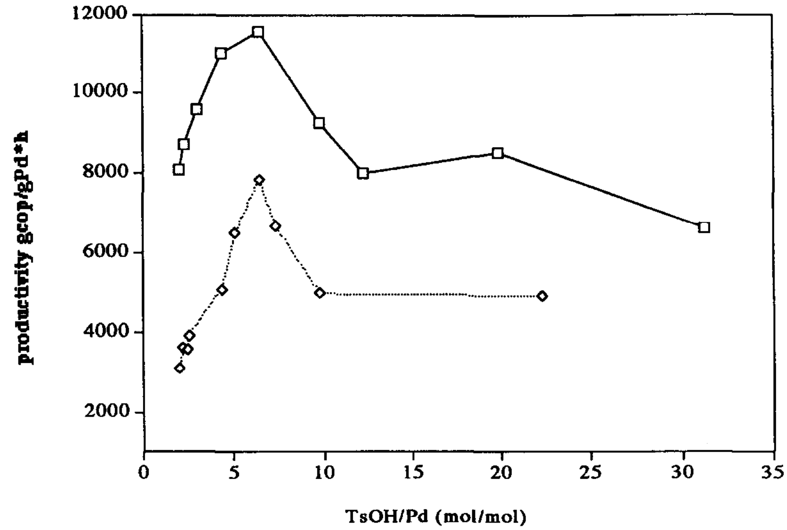

Fig. 4. Influence of the dppp/Pd ratio on the productivity. Run conditions: pressure: dotted line 45 atm, solid line 60 atm; temperature: 90°C; MeOH: dotted line 50 ml; solid line 80 ml; [Pd]: dotted line 5.6×10^{-5} mol · l^{-1}, solid line 4.5×10^{-5} mol · l^{-1}; Pd/dppp = 1/1 (mol/mol); $[H_2O]$ dotted line 100 ppm; solid line 800 ppm, (w/w); reaction time: 2 h.

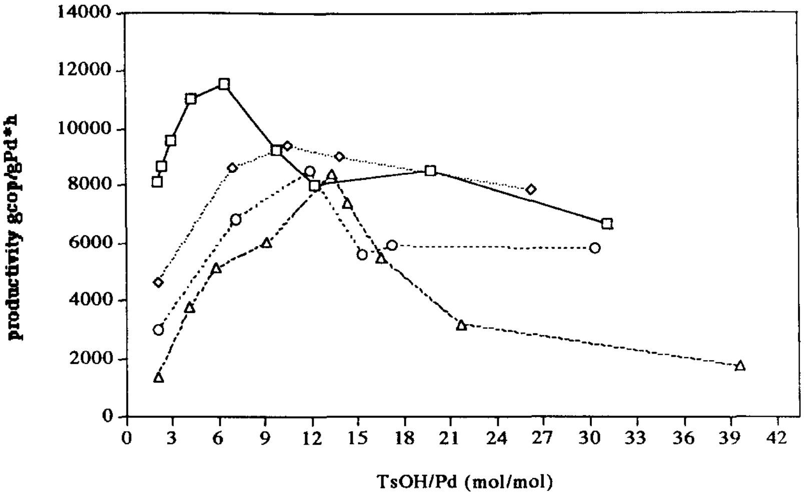

Fig. 5. Influence of the TsOH/Pd ratio on the productivity at different water concentrations. Run conditions: pressure: 60 atm; temperature: 90°C; MeOH: 80 ml; [Pd]: 4.5×10^{-5} mol · l^{-1}; Pd/dppp = 1/1 (mol/mol); [H_2O]: □ 800 ppm, ◇ 2650 ppm, ○ 4100 ppm, △ 5100 ppm, (w/w); reaction time: 2 h.

higher concentration of acid the productivity decreases sharply.

The beneficial effect of the acid may have several origins. The acid may increase the concentration of $[Pd–H]^+$ species through the equilibrium (10) which reactivates the complexes of Pd(0) which inevitably form in the reducing reaction medium. Moreover, as already mentioned, the acid shifts equilibria of the type (7) towards more active monomeric species.

The fact that the productivity decreases when the acid is added in relatively large amounts may be due to the possibility that the TsO^- anion competes with the monomers and with H_2O for the coordination to the metal. As a matter of fact, in the cationic complex $[Pd(dppp)(H_2O)(TsO)](TsO)$ a TsO^- anion is coordinated to the metal [24]. In addition, in the presence of a relatively high concentration of the acid there might be formation of neutral

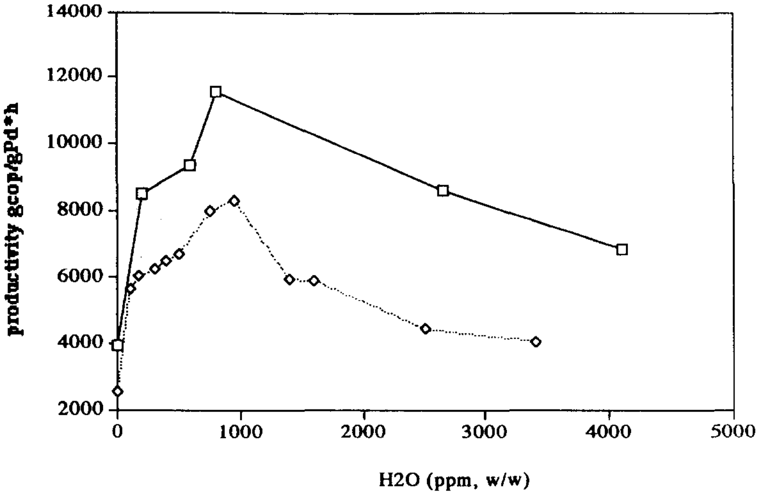

Fig. 6. Influence of the water concentration on the productivity at different TsOH/Pd ratio. Run conditions: pressure: 60 atm; temperature: 90°C; MeOH: 80 ml; [Pd]: 4.5×10^{-5} mol · l^{-1}; Pd/dppp = 1/1 (mol/mol); reaction time: 2 h.

hydride complexes of the type Pd(dppp)H(TsO) which may be consumed by a reaction with the acid with evolution of hydrogen. Relevant to this suggestion, it was found that the cationic hydride complex $[Pd(PPh_3)_3H]^+$, which forms in situ from the '$Pd(AcO)_2/PPh_3/CH_3COOH/H_2O$' system and which plays a key role in both the catalytic WGSR and the catalytic hydrocarbonylation of ethylene to diethylketone, is resistant to the attack of the acid when in the presence of a relatively high concentration of water ($\geq 30\%$), while it undergoes protonolysis with evolution of hydrogen when the water content is below 20%. It was proposed that the cationic hydride undergoes equilibrium (15), which is shifted towards a more favourable covalent neutral hydride unstable to protonolysis [32]:

$$[Pd(PPh_3)_3H]^+X^- \underset{PPh_3}{\overset{-PPh_3}{\rightleftharpoons}} \underset{(7)}{Pd(PPh_3)_2HX} \qquad (15)$$

$$(7) + HX \rightarrow Pd(PPh_3)_2X_2 + H_2 \qquad (16)$$

Fig. 5 shows that the maximum of productivity is shifted towards higher TsOH/Pd ratio on increasing H_2O concentration. This result gives further support to the suggestion that TsO^- and H_2O compete with the monomers for coordination to the metal.

In Fig. 6 the productivity as a function of H_2O concentration is shown at two different TsOH/Pd ratios.

2.1.4. *Influence of p-benzoquinone on the productivity*

As already mentioned, in the reaction medium palladium is present as both Pd(0) and Pd^{2+} species, and probably Pd(I) species of the type of the hydridecarbonyl dimer (**5**) [30,37–39]. In this system, BQ can oxidize Pd(0) to Pd(II) [40] and it can transform a $[Pd\text{–}H]^+$ species into a $[Pd\text{–}OCH_3]^+$ species [5], as schematized by reactions (17) and (18), respectively:

$$Pd(0) + BQ + 2H^+ \rightarrow [Pd]^{2+} + H_2BQ \xrightarrow[-H^+]{BQ, MeOH} [Pd\text{–}(OMe)]^+ \qquad (17)$$

$$[Pd\text{–}H]^+ + BQ + MeOH \rightarrow [Pd\text{–}(OMe)]^+ + H_2BQ \qquad (18)$$

As discussed above, it is likely that the promoting effect of H_2O and of TsOH, when present in convenient amounts, is due to the possibility that they are able to increase the concentration of active $[Pd\text{–}H]^+$ species that start the catalytic cycle. In the presence of very little amounts of H_2O and when the ratio Pd/TsOH = 2 the productivity is rather low. However, it significantly increases when the ratio is 7/1

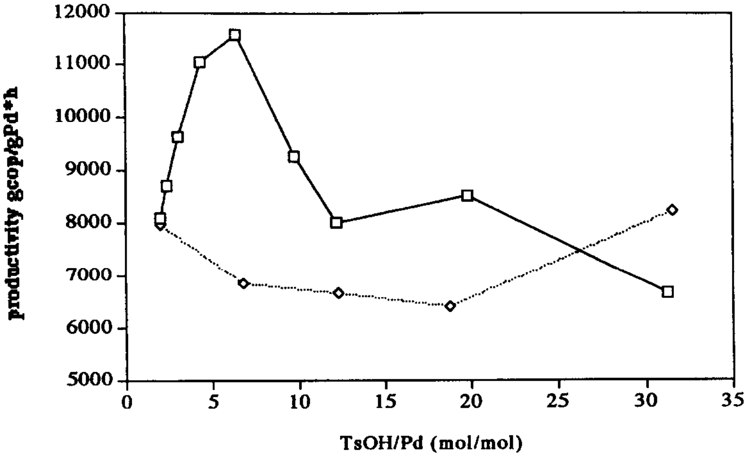

Fig. 7. Influence of *p*-benzoquinone on the productivity. Run conditions: as those reported under Fig. 4, solid line, except for the presence of BQ (initial amount 100 mg).

(from 2500 to 4000 g-pol/g-Pd · h under the conditions relevant to Fig. 6). These facts suggest that when water is present in very low concentration and when the acid is not in excess, the concentration of active $[PdH]^+$ species is either relatively low and/or the concentration of inactive Pd(0) species are relatively high (cf. equilibrium (11) and (13b)). As already mentioned, under these conditions the catalytic cycle may start from a $[Pd-(OCH_3)]^+$ species and/or from a hydride that forms from this species through reaction (12).

We found that when the copolymerization is carried out in the presence of a relatively high amount of BQ (BQ/Pd = 330 mol/mol) the productivity is much increased. For example under the conditions reported in Fig. 3, dotted line, the productivity passes from ca. 2000 g-pol/g-Pd · h to 6500 g-pol/g-Pd · h when BQ is present. This value is close to the one of maximum productivity (7400 g-pol/g-Pd · h). This fact suggests that BQ restores the catalytically active $[Pd(OCH_3)]^+$ species through reactions (16) and (17). Instead, when the copolymerization is carried out under the experimental conditions in which the productivity reaches a maximum (11500 g-pol/g-Pd · h, Fig. 7), but in the presence of BQ (BQ/Pd = 260), the productivity decreases to 6850 g-pol/g-Pd · h. This observation can be interpreted as the consequence of the possibility that in the presence of BQ the $[Pd-H]^+$ species, which are present in relatively high concentration under the conditions of maximum productivity, are transformed into $[Pd-(OCH_3)]^+$ species according to reaction (18). It is noteworthy to observe that when the copolymerization is carried out in the presence of BQ the productivity is levelled off to an average value of 7000 g-pol/g-Pd · h, irrespective of whether the copolymerization is carried out under the conditions of either high or low productivity. Moreover, in the presence of BQ the copolymerization is a stoichiometric reaction with respect to BQ (based on end groups) [5]. Thus, in this case the polymer originates from the initial insertion of CO into a $[Pd-(OCH_3)]^+$ bond. The process is made catalytic through the oxidation of the Pd(0) species, which forms in the final step of the catalytic cycle, by BQ which regenerates the $[Pd-(OCH_3)]^+$ species with formation of reduced BQH_2 (reaction (19)):

$$[Pd-(OCH_3)]^+ \xrightarrow{CO} [Pd-(COOCH_3)]^+ \xrightarrow{n(C_2H_4,CO)} [Pd-(COC_2H_4)_n(COOCH_3)]^+ \xrightarrow{CH_3OH} Pd(0) + \text{polymer II} + H^+ \qquad (19)$$

$$Pd(0) + H^+ + BQ + MeOH \rightarrow [Pd-(OMe)]^+ + H_2BQ$$

As a final comment it is worth observing that in the case of the synthesis of ketones by hydrocarbonylation of an olefin catalyzed by the system '$Pd(AcO)_2/PPh_3/CF_3COOH$', it was found that the rate of ketone formation is equal to the rate of CO_2 evolution. It was proposed that the catalytic cycle starts from a $[Pd-H]^+$ species and ends by protonolysis of intermediate (**8**) to yield the ketone and a PdX_2 species:

$$[Pd-H]^+ \xrightarrow{C_2H_4} [Pd-(C_2H_5)]^+ \xrightarrow{CO} [Pd-(COC_2H_5)]^+ \xrightarrow{C_2H_4} \underset{(\mathbf{8})}{[Pd-(C_2H_4COC_2H_5)]^+} \xrightarrow{HX} PdX_2 + C_2H_5COC_2H_5 \qquad (20)$$

The reaction is made catalytic through the interaction of CO and H_2O with the metal center, with regeneration of the hydride and concomitant evolution of CO_2 (reaction (13)) [31,32]. In other words, CO_2, which formally arises from the oxidation of CO with H_2O, is stoichiometric with respect to the ketone.

3. Experimental

3.1. Reagents

Methanol was purchased from Baker (purity > 99.5%, 0.01% of water). *p*-Toluenesulfonic acid (monohydrate, 99%) and trimethylorthoformate were supplied by Janssen; the ester was distilled prior use. Palladium(II) acetate and 1,3-bis(diphenylphosphine)propane were Aldrich products. Carbon monoxide and ethylene were supplied by SIAD Company ('research grade', purity > 99.9%).

3.2. Equipment

The catalyst components were weighted on a Sartorious Micro balance (precision 0.001 mg). Gas chromatographic analysis was performed on a Hewlett Packard Model 5890, Series II chromatograph fitted with a 2.9 m 510–1100 mesh silica gel column.

3.3. Carbon monoxide–ethylene copolymerization

The copolymerization reactions were carried out in a magnetically driven stainless steel autoclave (AISI 316) of ca. 250 ml. 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.

In a typical experiment, 1.15 mg of dppp, 0.63 mg of $Pd(AcO)_2$, and 1.16 mg of TsOH (dppp/Pd/TsOH = 1/1/2) were dissolved into 50 ml of MeOH containing a known amount of bidistilled water. The autoclave was pressurized at room temperature by ca. 30 atm of the two gasses supplied as a 1/1 mixture from a tank reservoir. The autoclave was then heated to 90°C during ca. 15 min. The pressure was then adjusted to the desired value (typically 45 atm total pressure) and maintained constant throughout the experiment (2 h) by continuously supplying the gasses from the reservoir. At the end of the experiment the pressure was quickly released while cooling the autoclave. The product slurry was filtered, washed with MeOH and dried under vacuum at 80°C.

The uptake of the feed was measured by following the pressure drop in the reservoir. During the reaction period the rate of copolymerization was approximately constant. The catalyst activity was calculated from the total gas fed during the reaction period.

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