

Synthesis, characterization and X-ray structure of $[\text{Pd}(\text{SO}_4)(\text{dpppp})] \cdot \text{H}_2\text{O}$, a catalyst for the CO-ethene copolymerization [dpppp = 1,3-bis(diphenylphosphino)propane]

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Abstract

The title complex has been synthesized by first reacting dpppp with $\text{Pd}(\text{AcO})_2$ in acetone and then with NaHSO_4 in water. It has been characterized by IR, NMR and X-ray diffraction studies. The ^{31}P NMR spectrum in DMSO shows a singlet at 16.62 ppm indicating that the two P atoms are equivalent and that the sulfate anion is weakly coordinating. The X-ray structure shows that the Pd atom is surrounded in an almost regular square planar environment by the two P atoms and by two O atoms of the sulfate anion and that the neutral complex is accompanied by a water molecule of crystallization. The Pd–P distances (2.217(1) and 2.233(1)) and the P–Pd–P angle (90.78(3)°) are close to those found in other complexes where the chelating diphosphine is the same. Also the Pd–O distances and the O–Pd–O bond angle are comparable to those of other relevant chelating ligands.

In MeOH, the title complex, in combination with H_2SO_4 , catalyses the CO-ethene copolymerization. The productivity reaches a maximum upon increasing the $\text{H}_2\text{SO}_4/\text{Pd}$ ratio up to ca. 470 (7650 g of polyketone/g Pd h at 90 °C and 45 atm, CO/ethene 1/1). The viscosity of the polyketone passes through a maximum of 0.95 dL/g in *m*-cresol when the above ratio is ca. 100. It has been proposed that acid promotes the copolymerization process by destabilizing the β - and γ -chelates intermediates involved in chain growing process, thus favoring the insertion of the monomers. At relatively high acid concentration the lowering of productivity and viscosity suggests that the sulfate anion competes with the monomers for the coordination to the metal center.

In $\text{H}_2\text{O}-\text{CH}_3\text{COOH}$ as a solvent the productivity strongly depends on the $\text{H}_2\text{O}/\text{CH}_3\text{COOH}$ ratio, as it passes through a maximum of 12000 g polymer/g Pd h in the presence of ca. 60% of H_2O . The productivity is significantly lower than that found when the acetate and chloride analogues are used (27000 g polyketone/g Pd · h). Thus, it is likely that the sulfate anion assists significantly the copolymerization process even though the concentration of $\text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^-$ is much preponderant.

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1. Introduction

Cis-coordinated diphosphine cationic complexes of Pd(II) can be highly active catalysts in the carbonylation of ethene to a wide spectrum of important products ranging from high molecular weight perfectly alternating

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polyketones (PK) or cooligomers, or lower carbonylated derivatives down to monocarbonylated products such as diethyl ketone (DEK) or propanoic acid and its esters [1–3]. PK represents a new class of melt-processable thermoplastic with interesting physical–mechanical properties, biodegradability, impermeability towards gases and organic solvents [4]. Mixtures of low molecular weight products and DEK can find large use as low volatility “green” solvents [5]. Methyl propanoate (MP) is a potential intermediate to methyl methacrylate, an important monomer produced annually as a multimillion tonne scale worldwide [6].

The reactions are usually performed using MeOH as solvent, which acts also as a source of Pd–H or Pd–OCH₃ species, which start the catalysis [7]. Monocarbonylated products form through the so called “hydride” mechanism, which involves the insertion of the olefin into a Pd–H bond with formation of a Pd–alkyl bond, followed by the insertion of CO into the Pd–alkyl intermediate with formation of a Pd–acyl species, which undergoes alcoholysis or hydrolysis to the ester or the acid with reformation of the Pd–H species starting the catalytic cycle [8–11]. DEK forms when the insertion of a second molecule of ethene into the Pd–acyl bond occurs with formation of a Pd–alkylacyl intermediate, followed by protonolysis [12–14]. If the Pd–alkylacyl intermediate undergoes successive multiple sequential insertions of CO and ethene the process of chain growing proceeds through the intermediate formation of β - and γ -chelates till termination occurs with formation of cooligomers or of PK [1–3,15]. Termination occurs via alcoholysis or protonolysis. Protonolysis by MeOH yields the polymer and a Pd–OCH₃ species, which can start the so called “carboalkoxy” mechanism, which involves the insertion of CO with formation of a Pd–COOCH₃ species followed by successive multiple sequential insertion of ethene and CO till termination [16].

Cis-coordination is ideal for promoting the insertion reactions. In order to ease the coordination of the monomers and the subsequent chain growing process, the cationic charge of the metal center has to be balanced by a non- or weakly-coordinating anion, conjugated base of a strong acid, for example TsOH (*p*-toluenesulfonic acid), HBF₄, HPF₆, CF₃COOH, CF₃SO₃H [7].

The selectivity of the carbonylation reaction depends mainly on the nature of the ligand. C₃-bridged diphenylphosphine of the type reported on the title, or other diaryl analogues, for example with *ortho*-methoxy substituents on the phenyl rings, are highly active in the copolymerization process [17], whereas bulkier diphosphines such as *t*-BuP(CH₂)₃PBu-*t* or 1,2-bis[(di-*tert*-butyl)phosphinomethyl]benzene are very active and selective in promoting the methoxycarbonylation to MP [8–11,17]. That steric bulk plays a role of paramount importance in controlling the selectivity of the reaction is also well illustrated by the results obtained using cationic Pd(II) complexes of 1,1'-bis(dialkylphosphino) fer-

rocene ligand, as when alkyl = methyl the catalyst is very active in promoting high molecular weight PK, whereas when alkyl = ethyl lower molecular weight PK are obtained, and when alkyl = *i*-propyl the products are MP and DEK [18].

Usually the catalyst is used in combination with an excess of acid (acid/Pd = 10–50) and of an organic oxidant such as benzoquinone (BQ/Pd = 50–100), to prevent deprotonation of the active Pd–H species and to reoxidize less active Pd(I) and Pd(0) species which unavoidably form during the course of the catalysis. Possible deactivation paths have been delineated in [2].

The influence of the anion has been less studied, though the anion plays also a role in the catalysis. For catalysts which promote the formation of low molecular weight products the selectivity may depend dramatically from the nature of the anion, as in the case of ethane-bridged bis(phosphabicyclononane)-based catalyst that changes from a low molecular weight polymer to MP when the counter-anion is CH₃SO₃[−] or propanoate, respectively [19].

The coordinating capacity depends not only on the nature of the anion, but also on that of the solvent. Polar solvents help the dissociation of the anion from the cationic active catalyst, thus favoring the polymerization process. This is well illustrated by comparing the activity of the catalysts [PdX₂(dppp)] (X = TfO, TsO, TFA, AcO, Cl). In MeOH the activity is comparable when X is weakly coordinating like TfO, TsO, TFA (ca. 7000–6000 g polymer/g Pd h at 90°, 45 bar, CO/ethene = 1/1). When X = AcO or Cl the catalyst is ineffective [7], but becomes very active when used in H₂O–AcOH, ca. 40–50% molar ratio, 27000 g polymer/g Pd · h, under the conditions just reported, in spite of the lower solubility of the monomers in this medium [20,21].

Also the activity of water-soluble catalysts based on the hydrophilic bidentate phosphines is significantly influenced by the nature of the anion [22–28].

The influence of the concentration of the acid has also received less attention, though it has been reported that for the Pd(AcO)₂ precursor in combination with an excess of PPh₃ or with the monosulfonated derivative PPh₂Ph SO₃H, in acetic acid and in the presence of TsOH (Pd/P/TsOH = 1/8/80–800, 90 °C, 1–50 bar), the reaction switches from monocarbonylation with formation of propionic acid to oligocarbonylation products and to polyketones as the pressure and concentration of TsOH increase. The yield in polyketones also increases upon increasing the acidity [29,30]. A similar acid effect has been found with the dtbpe-based catalyst in MeOH for the production of DEK in the presence of excess acid, as the selectivity lowers from 99% DEK to up to ca. 33%, ca. 60% being cooligomers [14].

In this article, we report the synthesis and characterization of the title complex and its catalytic activity in the CO-ethene copolymerization in MeOH at different H₂SO₄/Pd ratio or H₂O–CH₃COOH as solvents.

2. Experimental

2.1. Reagents

Methanol (purity >99.5%, 500 ppm water) and acetic acid (100%, glacial) 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 complexes $[\text{PdX}_2(\text{dppp})]$ ($\text{X} = \text{Cl}$, AcO , TsO) were prepared as reported in literature [31,32]. Carbon monoxide and ethylene were supplied by SIAD Company ('research grade', purity >99.9%).

2.2. Equipment

Gas-chromatographic analysis of the gas phase was performed on a Hewlett–Packard Model 5890, Series II chromatograph fitted with a 18 ft \times 1/8 SS Silica Gel, 60/80 packed column.

The limiting viscosity number (LVN) measurements were performed on a capillary viscosimeter at 25 °C using *m*-cresol as solvent.

IR spectra were recorded in nujol mull on a Nicolet FTIR instrument mod. Nexus. ^1H and ^{31}P NMR spectra of complex (I) were recorded on a Bruker AMX 300 spectrometer equipped with a BB multinuclear probe operating in the FT mode at 300 and 121.442 MHz for ^1H and ^{31}P , respectively.

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

The X-ray diffraction analysis were recorded on a STADI4 CCD automated diffractometer.

2.3. Synthesis of $[\text{Pd}(\text{SO}_4)(\text{dppp})] \cdot \text{H}_2\text{O}$ (I)

An acetone solution of dppp was added dropwise, under stirring, at r.t., to an acetone solution of $\text{Pd}(\text{AcO})_2$ (3 mL, 112 mg, 0.50 mmol). The resulting yellow suspension was allowed to stir for ca. 20. Upon addition of 160 mg of $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ (1.15 mol), dissolved in 1 mL of H_2O , the yellow solid first dissolved and then precipitation of a pale yellow solid was observed. The suspension was stirred for ca. 30 min and then filtered. The yellow solid was washed with acetone–water (5/2), ethyl ether and dried on vacuum. Yield 284 mg, 90%. Suitable crystal for X-ray structure determination have been obtained by recrystallization from $\text{MeOH}-\text{CHCl}_3$ –petrol ether. *Anal.* Calc. for $\text{C}_{27}\text{H}_{28}\text{O}_5\text{P}_2\text{S}$: C, 51.21; H, 4.46; S, 5.07. Found: C, 51.13; H, 4.54; S, 4.59%.

2.4. Carbon monoxide-ethene 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, 0.540 mg of (I) (8.57×10^{-4} mmol) was added to 80 mL of MeOH (containing H_2SO_4) or of $\text{AcOH}-\text{H}_2\text{O}$ ($\text{H}_2\text{O} = 55\%$, mol/mol) contained in the bottle placed in the autoclave. The autoclave was pressurized at room temperature with ca. 0.5 MPa of the two gasses 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 4.5 MPa total pressure) and maintained constant throughout the experiment (1 h, rate stirring 700 rpm) by continuously supplying the gasses 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.

2.5. X-ray diffraction analysis

A crystal suitable for the X-ray analysis was mounted on the top of a glass fiber, coated with epoxy resin, and transferred to a STADI4 CCD automated diffractometer. Data were collected at room temperature, using graphite monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$), and corrected for Lorentz, polarization and absorption effects.

The structure was solved by means of the heavy-atom methods, using the SHELXTL-NT package [33,34], and was refined by full-matrix least-squares methods on F^2 with SHELXL-97 [35]. All non-hydrogen atoms were refined anisotropically; hydrogen atoms (apart from those of the water molecule) were placed in calculated positions and refined as riding model. A summary of crystal and refinement data is reported in Table 1, while Table 2 lists some selected interatomic distances and angles.

Table 1
Summary of crystal and structure refinement

Empirical formula	$\text{C}_{27}\text{H}_{28}\text{O}_5\text{P}_2\text{PdS}$
Formula weight	632.89
Crystal system; space group	monoclinic; $P2_1/c$ (No. 14)
a (Å)	9.983(2)
b (Å)	15.634(3)
c (Å)	17.551(4)
β (°)	95.92(3)
V (Å ³)	2724.6(9)
Z ; D_{calcd} (Mg m^{-3})	4; 1.543
λ (Å), μ (cm^{-1})	0.71073; 9.11
θ Range (°)	3.3–29.5
Reflections collected	6971
Reflections observed ($I > 2\sigma(I)$)	5037
Data/parameters ratio	6971/325
R_1^a (observed reflections)	0.031
wR_2^b (observed reflections)	0.062
Goodness-of-fit on F^2	0.939
Largest peak ($e \text{ \AA}^{-3}$)	0.89

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b wR_2 = \left[\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right]^{1/2}$$

$$^c \text{GOF} = \left[\frac{\sum w(|F_o^2| - |F_c^2|)^2}{(N_{\text{obsd}} - N_{\text{params}})} \right]^{1/2}$$

Table 2
Selected bond distances (Å) and angles (°)

Pd–P(1)	2.217(1)	S–O(1)	1.519(2)
Pd–P(2)	2.233(1)	S–O(2)	1.523(2)
Pd–O(1)	2.097(2)	S–O(3)	1.438(2)
Pd–O(2)	2.093(2)	S–O(4)	1.444(2)
Pd–S	2.689(1)		
P(1)–Pd–P(2)	90.78(3)	Pd–P(1)–C(1)	116.64(9)
O(1)–Pd–O(2)	68.62(6)	Pd–P(2)–C(3)	114.81(9)
P(1)–Pd–O(2)	166.90(5)	Pd–O(1)–S	94.73(8)
P(2)–Pd–O(1)	170.27(5)	Pd–O(2)–S	94.76(8)

3. Results and discussion

3.1. Characterization and X-ray structure of complex (I)

The IR spectrum shows bands at 3625 and 3389 cm^{-1} for the stretching bands of H_2O [32] and at 1235, 1099 and between 900 and 850 cm^{-1} for the sulphate anion [36].

The ^1H NMR spectrum in deuterated DMSO shows one signal at 3.36 ppm (H_2O), a broad signal at 2.88 ppm (4H, PCH_2), and a multiplet at 1.97 ppm (2H, CH_2). The ^{31}P NMR in DMSO shows a singlet at 16.62 ppm and in $\text{CDCl}_3\text{-CD}_3\text{OD}$ a singlet at 18.45 ppm, thus indicating that the two P atoms are magnetically equivalent. The ^{31}P NMR of the related complexes $[\text{Pd}(\text{TsO})_2(\text{dppp})] \cdot 2\text{H}_2\text{O}$ [37] and $[\text{Pd}(\text{TsO})(\text{H}_2\text{O})(\text{dppp})](\text{TsO})$ [32] in CDCl_3 show a singlet in the same region, 16.0 and 17.5 ppm, respectively, whereas the analogous complex $[\text{Pd}(\text{CF}_3\text{COO})_2(\text{dppp})]$ shows a singlet at 11.56 ppm [38]. It has been also reported that addition of two equivalents of TsOH to an equimolar mixture of $\text{Pd}(\text{AcO})_2$ and dppp in acetone solution causes a downfield shift of the phosphorous signal from 11.1 to 17.5 ppm [7]. This deshielding of the P atoms has been attributed to the shift of electron density from the P atoms to a more electrophilic Pd centre which results upon replacement of the acetate anions by TsO^- [7]. Thus the position of the signal of complex (I) indicates that the P atoms are deshielded and that the sulphate anion is labile. This lability is likely to be related to the high catalytic activity of complex (I), comparable to that of the tosylate analogue (see below).

The X-ray structure shows that in the solid state the neutral complex is accompanied by a crystallization water molecule. An ORTEP [39] representation of the molecular structure of the complex, together with the employed numbering scheme, is illustrated in Fig. 1.

The environment of the Pd atom is almost regular square planar, and the chelate diphosphine ligand forms upon coordination a six-membered ring, assuming a *chair* (D_{3d}) conformation. To the best of our knowledge, this is the first example of a Pd(II) complex with a chelating sulfate dianion. A search in the Cambridge Crystallographic Database (CCD) [40] for square planar Pd(II) complexes showing the $(\text{P}^\text{II})\text{O}_2$ donor set and at least one oxygen bound to a sulfur atom ($\text{P}^\text{II}\text{P} =$ bidentate neutral phosphorous ligand) returned five entries [11,41,42]. The main geo-

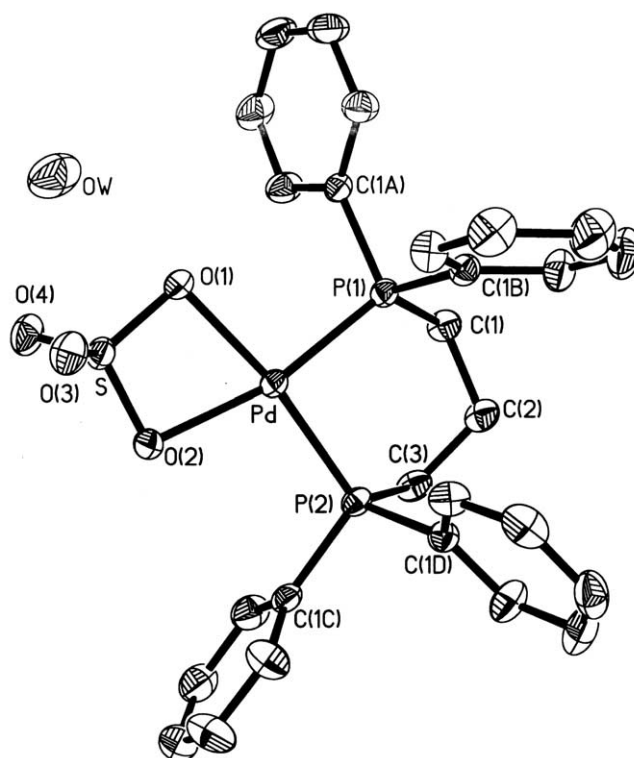


Fig. 1. The molecular structure of the complex; hydrogen atoms not shown for clarity. Thermal ellipsoids at the 40% probability level.

metrical parameters for the reported structures are listed in Table 3.

The Pd–P distances (2.217(1) and 2.233(1) Å) fit within the reported experimental range and are similar to those found in $[\text{Pd}(\text{OTf})(\text{H}_2\text{O})(\text{dppp})]$ (OTf) [42]; the Pd–O distances (2.097(2) and 2.093(2) Å) are very short and close to the values found in $[\text{Pd}(\text{OS}(\text{Me})\text{O})(\text{dppp})]_2$ (BAr_4)₂ [41] (2.078(5) and 2.088(5) Å). However, in the present complex the chelate ligand is dianionic and the formal oxidation state of sulfur is +6, while compound [41] is a dinuclear complex in which a monoanionic ligand bridges two Pd units and the formal oxidation state of sulfur is +2. If compound [41] is omitted, the Pd–O bond lengths found here are the shortest reported so far. This is likely due to the restraints imposed by chelation, or to the harder σ donor character of the dianionic ligand. The latter idea seems somewhat reinforced by looking at data listed in Table 3, where the S–O distances of the coordinating oxygens are ca. 0.06 Å longer than those of the non-coordinating ones. In this work, the lengthening grows to 0.09 Å, with the distances (1.519(2) and 1.523(2) Å) becoming the longest reported so far.

With respect to bond angles, the P(1)–Pd–P(2) angle (90.78(3)°) is similar to those reported in $[\text{Pd}(\text{OTf})(\text{H}_2\text{O})(\text{dppp})](\text{OTf})$ [42] and $[\text{Pd}(\text{OTs})(\text{H}_2\text{O})(\text{dppp})](\text{OTs})$ [32], and is also close to the average of 92.5° found in about thirty analogous Pd compounds [40]; on the other hand, the O(1)–Pd–O(2) angle is similar to that of the chelating methanesulfonate ligand in $[\text{Pd}(\eta^2\text{-MeSO}_3)(\text{d}^i\text{bpx})]$

Table 3
Geometrical parameters of reported square planar Pd(II) complexes

	Pd–P	Pd–O	S–O ^a	S–O ^b	P(1)–Pd–P(2)	O(1)–Pd–O(2)
[Pd(η^2 -SO ₄)(dppp)] · H ₂ O [this work]	2.217 (1) 2.233 (1)	2.097 (2) 2.093 (2)	1.519 (2) 1.523 (2)	1.438 (2) 1.444 (2)	90.78 (3)	68.62 (6)
[Pd(η^2 -MeSO ₃)(dtbpx)] (MeSO ₃)(MeSO ₃ H) [11] ^c	2.274 (2) 2.267 (2)	2.188 (4) 2.172 (4)	1.490 ^d 1.492 ^d	1.421 ^d	100.59 (6)	65.7 (1)
[Pd(OS(Me)O)(dppp)] ₂ (BAr ₄) ₂ [41] ^e	2.235 (2) 2.239 (2)	2.078 (5) 2.088 (5)	1.494 (5) 1.507 (5)		90.12 (7)	90.9 (2)
[Pd(OTf)(H ₂ O)(dppp)] (OTf) [42]	2.237 (1) 2.228 (1)	2.106 (4) ^c 2.159 (3)	1.469 (4)	1.411 (5) 1.425 (5)	90.98 (4)	86.1 (2)
[Pd(OTs)(H ₂ O)(dppp)] (OTs) [32]	2.236 (1) 2.236 (1)	2.138 (4) ^c 2.152 (3)	1.484 (3)	1.446 (4) 1.434 (5)	88.61 (4)	85.9 (1)

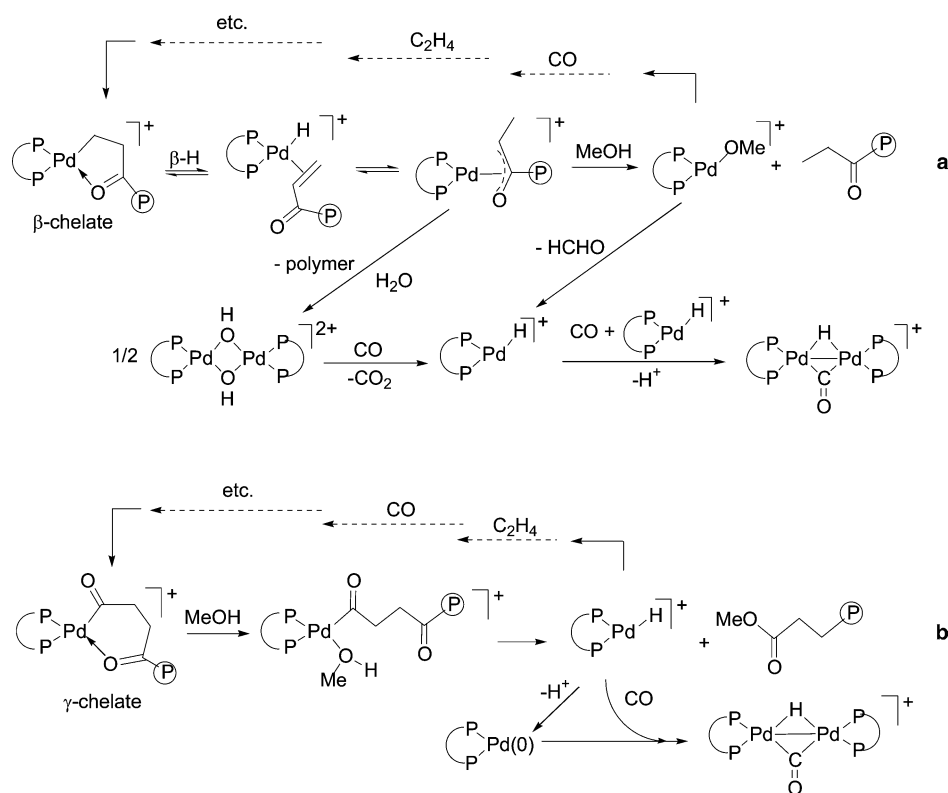
^a Refers to the coordinating oxygen(s).

^b Refers to non-coordinating oxygen(s).

^c Refers to the oxygen not bound to sulfur.

^d Data extracted from the Cambridge Crystallographic Database, standard deviations unavailable.

^e The reported metrical data refer to the one-half molecule defining the asymmetric unit.



Scheme 1. Catalytic cycles for the copolymerization process, with evidenced the termination step by protonolysis (a) and by methanolysis (b), and side reactions to less active Pd(0) and Pd(I) species.

(MeSO₃)(MeSO₃H) [11]. As for the nonbonding interactions, the crystallization water molecule is very loosely bound to the sulfate O(4) oxygen, with a O–O separation of 2.835 Å.

3.2. CO–C₂H₄ copolymerization

Complex (I) was used as catalyst precursor for the CO–C₂H₄ copolymerization in MeOH or in a mixture of

H₂O–CH₃COOH. In the first solvent the activity has been tested using the precursor in combination with H₂SO₄. In order to observe significant catalytic activity the acid must be used in excess. Under the condition reported in Fig. 3 the productivity reaches a maximum of ca. 7650 g of polymer/g of Pd h when the ratio H₂SO₄/Pd is ca. 470/1. This behavior is similar to that observed when the analogous acetate precursor is used in combination with formic acid, though in this case the productivity reaches a plateau of

ca. 7500 g polymer/g Pd h at a higher concentration of acid (HCOOH/Pd ca. 3000) [43]. Differently, the tosylate precursor $[\text{Pd}(\text{TsO})(\text{H}_2\text{O})(\text{dppp})](\text{H}_2\text{O})$ gives best results when the ratio TsOH/Pd is significantly lower (8/1) and in the presence of 800–1000 ppm of H_2O [44].

As already mentioned, a Pd-H or a Pd-OCH_3 species initiate the catalytic cycle [7]. In principle, these species should reform at the termination steps, which occur via methanolysis, or via protonolysis by MeOH or H_2O (always present in the solvent), as shown in the Scheme 1 [16].

Methanolysis can occur via inter- or intra-molecular nucleophilic attack by MeOH at the carbon atom of a Pd-acyl moiety and produces an ester end-group and a Pd-H^+ species, which may deprotonate with formation of less active $\text{Pd}(0)$ and dimeric species [45,46].

Protonolysis involves the reaction of a β -chelate moiety with methanol and produces a polymer with keto end-group and a Pd-OCH_3^+ species. The mechanism proposed to explain deuterium enrichment in the 2-position with respect to 1-position involves a pre-equilibrium of the β -chelate with its enolate isomer by a β -H elimination/hydride migration and protonation to the more nucleophilic oxygen atom to give an enol, which rearranges to the ketone [16,47]. When protonolysis occurs by H_2O , the binuclear complex $[\text{Pd}(\mu\text{-OH})(\text{P-P})]_2^{2+}$, which may form if excess acid is not used, reacts with CO with regeneration of a Pd-H^+ species after CO_2 evolution [48]. In turn the hydride may undergo deprotonation with formation of a less active dimer as shown in Scheme 1 [45,49,50].

The beneficial effect of H_2SO_4 on the productivity shown in Fig. 2 is probably due to the possibility that the acid inhibits the deprotonation of the active Pd-H^+ species which initiates the catalysis. The lowering of productivity at relatively high $\text{H}_2\text{SO}_4/\text{Pd}$ ratio suggests that the anion may compete with the monomers for the coordination to the metal center.

Since protonolysis is one of the chain termination reaction, a lowering of the molecular weight of the copolymer should be expected upon increasing the acid concentration. For the catalytic system $\text{Pd}(\text{AcO})_2/\text{dppp}/\text{CF}_3\text{COOH}$ it was also found that the molecular weight is not effected upon increasing the acid/ Pd ratio up to 100 [51]. It was concluded that enolate formation is the rate determining step.

However, the results obtained with the system complex (I)/ H_2SO_4 show that the viscosity significantly increases upon increasing the $\text{H}_2\text{SO}_4/\text{Pd}$ ratio up to 100 and that at higher ratio it decreases (see Fig. 2). These results suggest that at relatively high concentration of the acid the chain growing process may slow down because of the above mentioned competition between the sulfate anion and the monomers, whereas at relatively low acid concentration the rate of the copolymerization process increases upon increasing the acid concentration. We suggest that protonation of the oxygen atom of the coordinating keto groups might destabilize the β - or of the γ -chelates, thus favoring the insertion of the monomers. At this regard, it is worth mentioning that the insertion of ethene is believed to be the slow step of the copolymerization process [1].

As already mentioned the copolymerization is carried out also in the presence of an organic oxidant, such as BQ, which has the function to reoxidize the $\text{Pd}(0)$ and $\text{Pd}(\text{I})$ species. When the copolymerization is carried out in the presence of relatively high concentration of H_2SO_4 , the use of BQ is influent. In order to evidentiare a possible beneficial effect of BQ it is necessary to carry out the copolymerization with a relatively low acid/palladium ratio. Thus, for example when $\text{H}_2\text{SO}_4/\text{Pd} = 10$, the productivity increases from 4000 g polymer/g Pd h in the absence of BQ to 8000 g.

In $\text{H}_2\text{O-CH}_3\text{COOH}$ as a solvent the productivity strongly depends on the $\text{H}_2\text{O}/\text{CH}_3\text{COOH}$ ratio, as it passes through a maximum of 12000 g polymer/g Pd h in the presence of ca. 60% of H_2O (Fig. 3). The productivity is significantly lower than that found when the acetate and

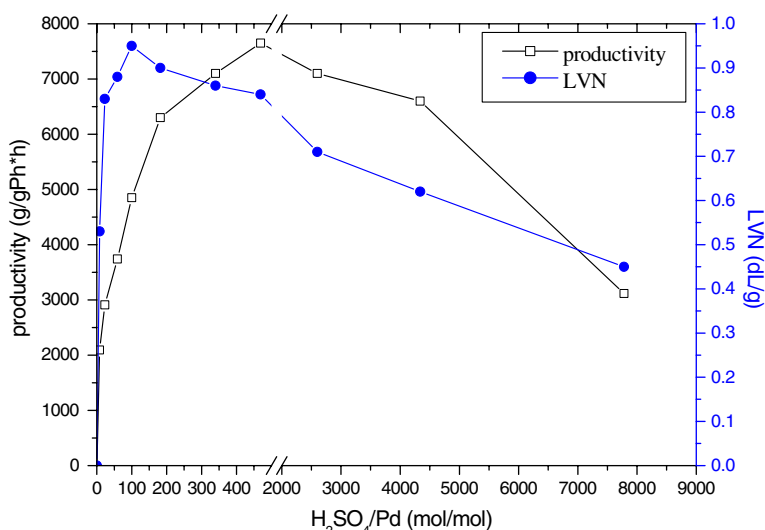


Fig. 2. Effect of H_2SO_4 addition on the productivity and on the LVN in MeOH as solvent Run conditions: $[\text{Pd}(\text{SO}_4)(\text{dppp})] \cdot \text{H}_2\text{O} = 2.8 \times 10^{-3}$ mmol; $P = 4.5$ MPa ($\text{CO}/\text{C}_2\text{H}_4 = 1/1$, at the working temperature); $T = 90$ °C; $\text{MeOH} = 80$ mL; reaction time = 1 h; stirrer = 700 rpm.

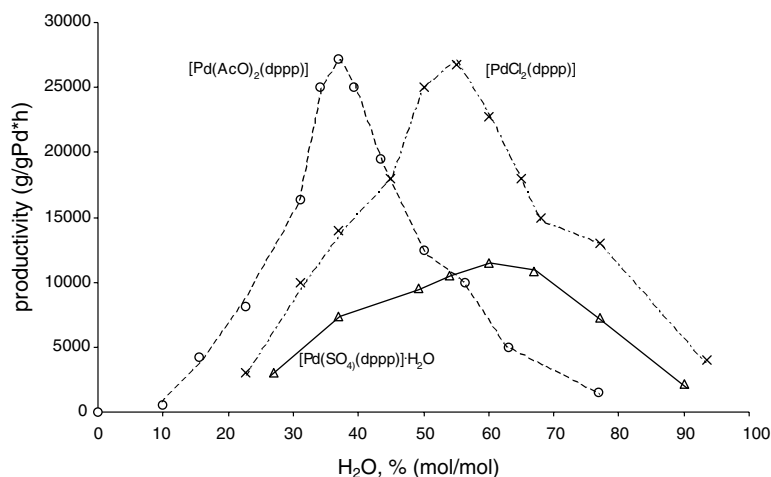


Fig. 3. Effect of the concentration of water on the productivity in acetic acid as solvent. Run conditions: $[\text{Pd}(\text{SO}_4)(\text{dppp})] \cdot \text{H}_2\text{O} = 8.5 \times 10^{-4}$ mmol; $P = 4.5$ MPa ($\text{CO}/\text{C}_2\text{H}_4 = 1/1$, at the working temperature); $T = 90$ °C; H_2O – AcOH : 80 mL; reaction time = 1 h; stirrer = 700 rpm. For comparison, the productivities obtained using the precursors $[\text{Pd}(\text{AcO})_2(\text{dppp})]$, $[\text{PdCl}_2(\text{dppp})]$ (see [20,21], respectively) are also shown.

chloride analogues are used [20,21]. Thus, in this solvent, it is likely that the sulfate anion assists significantly the copolymerization process even though the concentration of $\text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^-$ is much preponderant.

The relatively high molecular weight of the polymer prevented to establish the nature of the end groups. The fact that the copolymerization process occurs with concomitant CO_2 evolution suggests that the catalytic cycle starts from a hydride and that termination occurs via protonolysis by H_2O or H_3O^+ with formation of $\text{Pd}-\text{OH}^+$ or $\text{Pd}-\text{OH}_2^{2+}$, which regenerate the starting $\text{Pd}-\text{H}^+$ species upon interaction with CO followed by evolution of CO_2 according to a reaction strictly related to the water gas-shift reaction [52–54]. CO_2 evolution has been observed also in the case of the copolymerization promoted by $[\text{PdX}_2(\text{dppp})]$ in H_2O – AcOH ($X = \text{AcO}, \text{Cl}$) [20,21].

The high activity may be due to the possibility that the acid and H_2O prevent deprotonation/dimerization of the active hydride with formation of dimeric species of the type shown in Scheme 1, thus ensuring a relatively high concentration of the most active species. Moreover, also in this case the acid through protonation of the oxygen atom of the coordinating keto group of the β - or γ -chelates may favors the insertions of the monomers in the process of chain growing.

The viscosity of the copolymer obtained under conditions of highest productivity (H_2O in $\text{CH}_3\text{COOH} = 60\%$) is 0.65 dL/g, in line with the values found when MeOH is used as solvent.

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