Catalytic conversions in water
Part 1l: Highly active water-soluble palladium-catalysts in the hydrocarboxylation of olefins and the alternating copolymerization of CO and olefins in water

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Abstract

Water-soluble palladium complexes of the sodium salt of trisulfonated triphenylphosphine (tppts, $P(C_6H_4\text{-}m\text{-}SO_3Na)_3$) catalyze the aqueous biphasic hydrocarboxylation of olefins. High catalytic activities were observed with small, sparingly water-soluble olefins such as propene (TOF > 2800 h^{-1} in the conversion to *n*- and isobutyric acid). Although selectivities (*n/iso* ratio) were rather moderate in the hydrocarboxylation of propene and 1-octene, high selectivities (> 99%) were observed in the conversion of isobutene or cyclopentene to 3-methylbutyric acid and cyclopentanecarboxylic acid, respectively. The water-soluble Pd catalyst based on the bidentate phosphine dpppr-s ($1,3\text{-}C_3H_6(P(C_6H_4\text{-}m\text{-}SO_3Na)_2)_2$) catalyzes the alternating copolymerization of CO and olefins to polyketones. Activities > 4.0 kg of copolymer per gram Pd per hour were found in the alternating copolymerization of CO and ethene. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Aqueous phase catalysis; Palladium; Tppts; Hydrocarboxylation; Alternating copolymerization; Olefins

1. Introduction

The increasing interest in water-soluble catalysts stems from the environmental benefits of using water as a solvent, and the facile catalyst recycling in liquid–liquid biphasic systems (see Refs. [1–3] for the latest reviews). Nevertheless, there are few examples of such systems that exhibit economically attractive activities.

We previously showed that the water-soluble palladium(0) complex, $Pd(tppts)_3$, catalyzes the carbonylation of benzylic-type alcohols such as benzylalcohol, 1-(4-isobutylphenyl)ethanol and the renewable base material 5-hydroxymethyl-furfural in aqueous media [4–7]. Although high selectivities were obtained, the reactivity of these systems remained low. In contrast, higher activities were observed in the biphasic hydrocarboxylation of olefins, e.g., the hydrocarboxylation of 4-isobutylstyrene to 2-(4-isobutylphenyl)propionic acid (ibuprofen) was eight times faster than the carbonylation of 1-(4-isobutylphenyl)-

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ethanol [8]. In the present paper, we report our further investigations of the biphasic hydrocarboxylation of olefins and the related alternating copolymerization of CO and olefins in the presence of Pd/dpppr-s in an aqueous medium.

2. Experimental

PdCl$_2$ and tppts were dissolved in 50 ml of distilled deoxygenated H$_2$O under an argon atmosphere to give the yellow [PdCl{tppts}$_3$]Cl within 25 min. A solution of Brønsted acid and the catalyst solution were charged into a 300-ml Hasteloy C autoclave quantitatively. The olefin was added and the argon was replaced by carbon monoxide after five pressurizing–depressurizing cycles. The appropriate pressure was applied and the autoclave was heated to reaction temperature. (In the case of ethene, propene and isobutene, after replacement of the argon atmosphere, the autoclave was pressurized via a stainless steel cylinder that contains the olefin.) The pressure was kept constant by adding carbon monoxide. After the reaction, the autoclave was cooled down immediately and the reaction gasses were vented. In the case of propene, isobutene and ethene, α-hydroxyisobutyric acid (standard) was added and the resulting solution was analyzed by HPLC directly. In the case of the other olefins, the products were extracted from the aqueous phase with an etheral solution of tetradecane (standard). Second extractions contained only traces of products. The organic layer was analyzed by GC immediately. In the alternating copolymerizations, the catalyst was prepared in situ by adding an aqueous solution of the ligand to a solution of [Pd(OTs)$_2$-(NCMe)$_2$] in water. After the reaction, the copolymers were filtered from the reaction mixture, washed with ethanol and dried in vacuo. For molecular weight determinations, the copolymer samples were dissolved in a mixture of 1,1,1,3,3,3-hexafluor-2-propanol and CDCl$_3$ (9:1) and analyzed with quantitative ^{13}C-NMR.
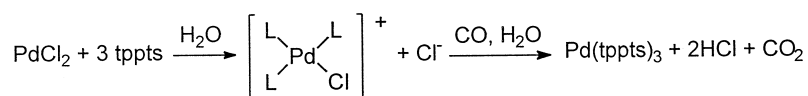
3. Hydrocarboxylations

We reported earlier that the biphasic hydrocarboxylation of olefins proceeds smoothly in the presence of the water-soluble Pd(tppts)$_3$ complex and a Brønsted acid cocatalyst such as p-toluenesulfonic acid [8]. 4-Isobutylstyrene was converted into 2-(4-isobutylphenyl)-propanoic acid (ibuprofen) in 62% conversion and 74% selectivity at 65°C and 50 bar. The hydrocarboxylation of styrene in the same system led to significantly higher catalytic activities which was explained by its higher solubility in the aqueous phase due to the absence of the hydrophobic isobutyl function. In the corresponding hydrocarboxylation of propene at 110°C, we observed turnover frequencies (TOFs) > 2500 mol product per mol catalyst per hour. In a direct comparison, the water-soluble Pd(tppts)$_3$ was found to be five times more active in this reaction than the classical Pd/PPh$_3$ catalyst in aqueous 1,4-dioxane (Scheme 1).

Two other groups independently discovered the biphasic hydrocarboxylation of olefins. Xie et al. [9] converted styrene into 2- and 3-phenyl-propionic acid in the presence of a water-soluble Pd(II)-complex based on tppts–H (P(C$_6$H$_4$-m-SO$_3$H)$_3$) and acetic acid as a cocatalyst. High conversions (up to 90%, 180 turnovers in 18 h) were obtained and a high selectivity towards the branched product ($n/iso = 44$ at 100°C, 100 bar CO) was observed. Tilloy et al. [10] also observed facile hydrocarboxylation of olefins with Pd/tppts in acidic media. The reactivity of their system, however, was substantially lower than ours, which is probably caused by the use of toluene as a second solvent which leads to an unfavorable distribution of the substrate between the organic and the aqueous
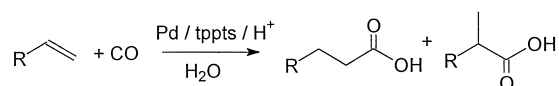
Scheme 1. The hydrocarboxylation of olefins in the aqueous phase.

$$PdCl_2 + 3\ tppts \xrightarrow{\ H_2O\ } \left[\begin{array}{c} L \diagdown \overset{\displaystyle L}{Pd} \diagup L \\ L \diagup \diagdown Cl \end{array} \right]^{+} + Cl^{-} \xrightarrow{\ CO,\ H_2O\ } Pd(tppts)_3 + 2HCl + CO_2$$

Scheme 2. The formation of $Pd(tppts)_3$ in situ.

phase. In another approach, heptakis-2,6-(O,O)dimethyl-β-cyclodextrin was found to be an effective phase transfer agent in the hydrocarboxylation of 1-decene [11].

3.1. Hydrocarboxylation of propene

The high reactivity of $Pd(tppts)_3$ in the hydrocarboxylation of propene encouraged us to further study this attractive system. We previously showed that the cationic complex, $[PdCl(tppts)_3]^{+}$, is formed when $PdCl_2$ is dissolved in a solution of tppts in water (Scheme 2) [12]. This complex is reduced by CO in 5 min at room temperature to afford the neutral complex $Pd(tppts)_3$, in quantitative yield, with the simultaneous formation of 2 equivalents HCl

[13]. The palladium-catalyzed hydrocarboxylation of olefins proceeds rapidly in such an acidic environment. In contrast, the catalyst decomposes rapidly under neutral or basic conditions.

Although the addition of an extra amount of a Brønsted acid is not essential, a high acid concentration is advantageous for the stability of the catalyst. When p-toluenesulfonic acid was used, the at least 10 mmol acid (150 equivalents per palladium) was generally needed to prevent the formation of metallic palladium at 110°C (Table 1, run 1/3). Adding more acid (e.g., 20 mmol or more) gave no further enhancement of activity. We tested a series of Brønsted acids in the hydrocarboxylation of propene. Good results were obtained in the case

Table 1
Pd/tppts-catalyzed hydrocarboxylation of propene. The effect of Brønsted acid

Run[a]	Brønsted acid	(mmol)	Conversion (%)	TOF (10^3 h^{-1})	Selectivity	
					n	iso
1/1[b]	–	(0.1)[c]	2	0.05	63	37
1/2	HOTs	(1.0)	32	0.96	59	41
1/3	HOTs	(10.0)	39	1.17	59	41
1/4	HOTs	(20.0)	39	1.17	59	41
1/5	HOTs	(30.0)	39	1.17	59	41
1/6	HOTs	(40.0)	42	1.26	59	41
1/7	H_2SO_4	(15.0)	40	1.20	59	41
1/8	H_2SO_4	(30.0)	41	1.21	60	40
1/9	HPF_6	(30.0)	41	1.22	60	40
1/10	H_3PO_3	(10.0)	30	0.91	60	40
1/11	H_3PO_3	(30.0)	31	0.94	61	39
1/12	$HOOCCF_3$	(30.0)	46	1.39	61	39
1/13[b]	$HOOCCH_3$	(30.0)	10	0.30	60	30
1/14	HCl	(30.0)	9	0.27	59	41
1/15	HBr	(30.0)	6	0.16	56	44
1/16	HI	(30.0)	1	0.05	43	57

[a] Reaction conditions: 11.8 mg $PdCl_2$ (0.067 mmol), 415.2 mg tppts · $3H_2O$ (0.667 mmol), Brønsted acid, 141.9 g total amount of catalyst solution ([Pd] = 0.47 mmol/l), 8.42 g propene (0.20 mol, olefin/Pd = 3000), temperature: 110°C, pressure: 50 bar CO, reaction time: 1 h.
[b] Pd^0 formation.
[c] Two equivalents of HCl (0.13 mmol) are formed during catalyst formation.

Table 2
Pd/tppts-catalyzed hydrocarboxylation of propene. The effect of the tppts/Pd molar ratio

Run[a]	Tppts/Pd molar ratio	Conversion (%)	TOF (10^3 h^{-1})	Selectivity	
				n	iso
2/1[b]	0	0	–	–	–
2/2[b]	4	29	0.85	61	39
2/3[b]	6	45	1.35	60	40
2/4	8	40	1.21	60	40
2/5	10	39	1.17	59	41
2/6	15	38	1.15	60	40

[a]Reaction conditions: see Table 1, except for the amount of tppts, 30 mmol p-toluenesulfonic acid.
[b]Formation of metallic palladium.

of H_2SO_4, HPF_6, H_3PO_4 and CF_3COOH, but the reactivity of the catalyst decreased substantially when Brønsted acids with coordinating anions were used in the order $OAc^- > Cl^- > Br^- > I^-$. We assume that this is caused by the occupation of free coordination sites on the palladium which inhibits the coordination of the reactants.

At a palladium concentration of 0.47 mmol/l ([HOTs] = 0.21 mol/l), 8 equivalents of tppts were required to prevent decomposition of the catalyst at 110°C and 50 bar (Table 2). Further increase of the tppts/Pd molar ratio had a minor negative effect on the activity of the catalyst. The reaction rate increased when higher temperatures and higher carbon monoxide pressures were applied. A remarkably high activity (TOF > 2800 h^{-1}) was observed at 130°C and 50 bar (Table 3, run 3/4).
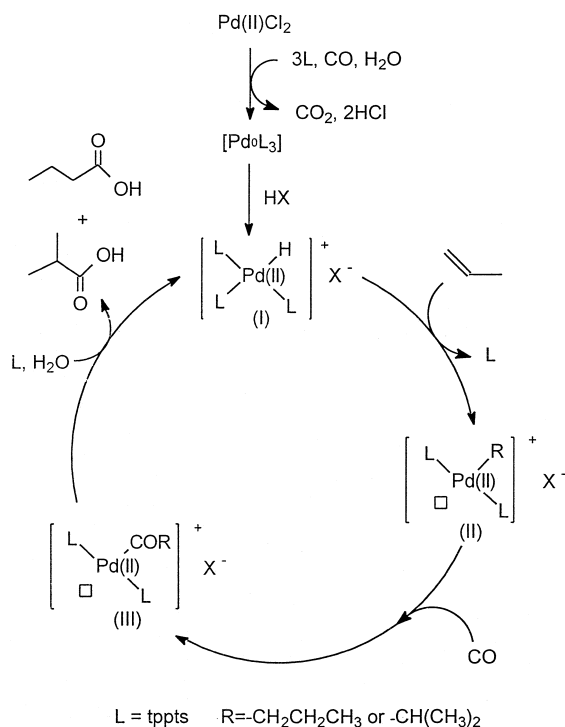
Unfortunately, the n/iso ratio did not lend itself to optimization by changing the reaction parameters. Under all conditions studied, the n/iso ratio remained between 1.4 and 1.7 for propene hydrocarboxylation.

We previously proposed the mechanism shown in Scheme 3 for the biphasic hydrocarboxylation of olefins [8]. Oxidative addition of the Brønsted acid to the neutral Pd(tppts)$_3$ complex affords a cationic palladium hydride complex. Subsequent olefin insertion into the palladium hydride bond followed by a migratory insertion of CO results in a palladium acyl species, which undergoes hydrolysis to afford the carboxylic acid and the cationic palladium hydride complex, which returns to the catalytic cycle. The mode of olefin insertion into the palladium hydride bond determines whether the linear or the branched product is formed. The analogues of intermediates I, II and III with PPh$_3$ instead of tppts have been identified with ^{1}H-, ^{13}C- and ^{31}P-NMR by Zudin et al. [14].

3.2. Hydrocarboxylation of 1-octene

While small carboxylic acids are water-soluble, carboxylic acids containing more than eight C atoms, e.g., nonanoic acid, are poorly soluble in water. Hydrocarboxylation of higher olefins would thus allow catalyst recovery after the reaction by a simple phase separation without the addition of organic solvents. However, the

Table 3
Pd/tppts-catalyzed hydrocarboxylation of propene. The effect of temperature and pressure

Run[a]	Temperature (°C)	Pressure (bar)	Conversion (%)	TOF (10^3 h^{-1})	Selectivity	
					n	iso
3/1	90	50	10	0.30	61	39
3/2	110	50	39	1.17	59	41
3/3[b]	120	50	40	2.40	60	40
3/4[b]	130	50	47	2.83	58	42
3/5	110	75	40	1.20	59	41
3/6	110	100	46	1.38	64	36

[a]Reaction conditions: see Table 1, 30 mmol p-toluenesulfonic acid.
[b]Reaction time: 30 min.

Scheme 3. The proposed mechanism for the Pd/tppts-catalyzed hydrocarboxylation of propene.

lower solubility of the olefin in the aqueous phase also leads to a much lower reactivity in the hydrocarboxylation of, e.g., 1-octene, compared to propene (Table 4). At 90°C, the catalyst was stable for at least 65 h (run 4/1), with

no metallic palladium being observed after the reaction. In contrast, at 100°C, the catalyst decomposed within 5 h. Besides hydrocarboxylation, we observed isomerization of 1-octene to internal octenes. Thus, in addition to the expected nonanoic and 2-methyloctanoic acid, 2-ethylheptanoic and 2-propylhexanoic acid were also formed. The latter two isomers, which are derived from hydrocarboxylation of 2-, 3-, or 4-octene, are present in much lower concentrations, consistent with the lower reactivity of secondary olefins towards hydrocarboxylation.

We reasoned that the low concentration of the substrate in the aqueous phase is responsible for the lower stability of the catalyst. By analogy with related systems in organic media [15], the hydrolysis of the Pd acyl bond is probably the rate determining step in the catalytic cycle with intermediate III being the predominant catalyst species. However, at extremely low olefin concentrations, the amount of the cationic Pd hydride, in equilibrium with $Pd(tppts)_3$ and lower ligated species, is likely to be higher. Such lower ligated complexes are less stable with respect to decomposition to palladium metal.

We attempted to facilitate the transport of 1-octene between the organic and the aqueous-phase by adding surfactants such as sodium

Table 4
Pd/tppts-catalyzed hydrocarboxylation of octenes

Run[a]	Olefin	Olefin/Pd molar ratio	Temperature (°C)	Pressure (bar)	Time (h)	Conversion (%)	Selectivity[d]				Isomeric octenes (%)
							a	b	c	d	
4/1	1-Octene	600	90	50	65	41	50	33	10	7	27
4/2	1-Octene	600	90	50	20	30	54	31	9	6	34
4/3[b]	2-Octenes[c]	600	90	50	20	0	–	–	–	–	100
4/4	2-Octenes[c]	150	70	50	20	3	0	60	24	16	97
4/5[b]	1-Octene	300	100	50	5	27	55	31	9	6	24
4/6	1-Octene	300	90	70	5	15	57	30	8	5	13
4/7	1-Octene	300	90	50	5	21	56	30	8	6	21
4/8	1-Octene	300	90	30	5	25	50	35	8	7	28
4/9	1-Octene	300	90	10	5	27	48	34	10	8	24

[a] Reaction conditions: see Table 1, 30 mmol p-toluenesulfonic acid.
[b] Formation of metallic palladium.
[c] 2-Octene cis/trans = 0.95.
[d] Selectivity towards carboxylic acids: (a) nonanoic acid, (b) 2-methyloctanoic acid, (c) 2-ethylheptanoic acid, and (d) 2-propylhexanoic acid.

Table 5

Initial reaction rates in the Pd/tppts-catalyzed hydrocarboxylation of other olefins to 3-methylbutanoic acid, cyclopentane carboxylic acid and propanoic acid

Run[a]	Substrate	HOTs (mmol)	Temperature (°C)	Conversion (%)	Selectivity	TOF (h^{-1})
5/1	Isobutene	30	90	6[c]	> 99% 3-methylbutanoic acid	193
5/2	Isobutene	10	90	8[d]	> 99% 3-methylbutanoic acid	252
5/3	*t*-Butanol	30	90	4	> 99% 3-methylbutanoic acid	116
5/4[e]	Cyclopentene	30	90	40	> 99% cyclopentanecarboxylic acid	81
5/5[f]	Ethene	30	110	45	72% propanoic acid	1340

[a] Reaction conditions: see Table 1, 30 mmol *p*-toluenesulfonic acid, 200 mmol substrate, reaction time: 1 h.
[b] Selectivity to carboxylic acids.
[c] Formation of *t*-butanol: 68%.
[d] Reaction time: 90 min, formation of *t*-butanol: 80%.
[e] Reaction time: 3 h, amount of olefin: 40 mmol.
[f] Formation of oligomeric keto-acids: $CH_3CH_2(COCH_2CH_2)_nCOOH$, $n = 1$: 6%, $n = 2$: 4%, $n = 3$: 1%.

dodecylsulfate or trimethylcetylammonium chloride or a phase transfer agent like heptakis-2,6-(O,O)dimethyl-β-cyclodextrin, but in our hands, these attempts were unsuccessful.

When a mixture of *cis*- and *trans*-2-octene ($cis/trans = 0.95$) was applied under the same reaction conditions, the catalyst decomposed rapidly. This is consistent with the notion (see above) that a low olefin concentration leads to catalyst decomposition, since the coordination of an internal olefin is less facile than a primary one. At a lower temperature (70°C), the catalyst remained intact and converted a small amount of the olefin mixture into the corresponding carboxylic acids, but the formation of either 1-octene or its hydrocarboxylation product, nonanoic acid, was not observed (run 4/4).

Increasing the carbon monoxide pressure had a negative effect on the hydrocarboxylation rate of 1-octene. In contrast with propene, the best result was obtained at only 10 bar carbon monoxide pressure. The selectivity towards the linear nonanoic acid increased when higher pressures were applied, but the optimum selectivity was still only 57%.

3.3. Selective hydrocarboxylation of isobutene and cyclopentene

The presence of an α-methyl group on the olefin had a dramatic effect on the selectivity.

Thus, isobutene was converted to 3-methylbutanoic acid in > 99% selectivity (Table 5), without any trace of the branched isomer 2,2-dimethylpropanoic acid being formed. Unfortunately, isobutene also undergoes acid-catalyzed hydration to *t*-butanol under the reaction conditions. Although this does not alter the outcome of the reaction (*t*-butanol is also selectively converted to 3-methylbutyric acid (run 5/3)), this competing hydration had a retarding effect on the hydrocarboxylation. By decreasing the amount of Brønsted acid and lowering the reaction temperature, the formation of *t*-butanol was suppressed to some extent, but this also resulted in a decrease in the stability and activity of the catalyst.

Cyclopentene underwent selective hydrocarboxylation to give cyclopentanecarboxylic acid in 40% yield (> 99% selectivity) after 3 h. Only traces of the hydrated substrate, cyclopentanol, were detected by GC measurements.
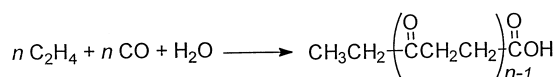
4. Alternating copolymerization of CO and olefins

Alternating copolymers of CO and olefins form a relative new family of materials, the so-called polyketones. There is a considerable

commercial interest in these materials since they have a high crystallinity, high mechanical strength, impermeability towards organic solvents and gases and they are prepared from the cheap monomers CO and ethene and/or propene [16]. Shell currently produces polyketones under the name Carilon (20,000 tons in 1996) and BP has announced the production of these materials under the name Ketonex. The catalysts that are used in these processes are generally Pd(II) complexes of a bidentate phosphine, e.g., 1,3-bis(diphenylphosphino)propane (dpppr) [17].

In our studies of the Pd(tppts)$_3$-catalyzed hydrocarboxylation of ethene, we observed, apart from the main product propanoic acid, the formation of some oligomeric keto-acids (Table 5, run 5/5, Scheme 4) which were identified by HPLC–MS measurements. Subsequently, we prepared the sodium salt of the sulfonated analogue of dpppr, dpppr-s (Fig. 1) via a new sulfonation procedure which is faster than the conventional method and reduces the amount of oxidized phosphine [18]. The water-soluble diphosphine was obtained in high yield (90%) and purity (98%). Indeed, replacement of tppts by dpppr-s leads to the smooth formation of the alternating copolymer of ethene and carbon monoxide that precipitates from the reaction mixture as a white solid (Table 6). Under the applied reaction conditions, we did not detect the presence of propionic acid or the oligomeric keto-acids as in the case of tppts.

The palladium-catalyzed alternating copolymerization of CO and ethene in an aqueous medium was previously reported by Jiang and Sen [19]. The catalytic activity observed (470 g copolymer per gram Pd in 18 h) was considerably lower than that observed with the Pd/dpppr system in methanol (> 6 kg copolymer per gram Pd per hour) [20] and this led them to

$$n\,C_2H_4 + n\,CO + H_2O \longrightarrow CH_3CH_2 \left(\overset{O}{\underset{\|}{C}}CH_2CH_2 \right)_{n-1} \overset{O}{\underset{\|}{C}}OH$$

Scheme 4. The alternating copolymerization of ethene and carbon monoxide, Pd/tppts: $n = 0,1,2,3$; Pd/dpppr-s: $\tilde{n} = 100$–200.
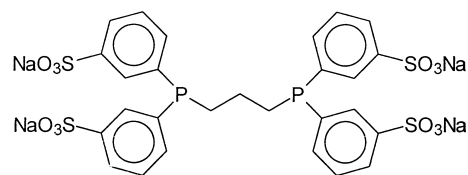

Fig. 1. The structure of dpppr-s.

conclude that the stronger coordination behavior of water to the palladium center hinders the incoming monomers, thus leading to low reaction rates. In contrast, using our pure, inorganic salt-free bidentate phosphine, in combination with a strong Brønsted acid cocatalyst, we observed catalytic activities of the same order as the organic system in methanol. Thus, under partly optimized reaction conditions, an activity larger than 4.0 kg copolymer per gram Pd per hour was observed [21].

The system shows many similarities with the hydrocarboxylation of olefins. The copolymerization does not take place in a neutral or basic environment and the reactivity improves when a Brønsted acid with weakly coordinating anions is added. Strongly coordinating anions inhibit the reaction, but the alternating copolymerization still proceeds in the presence of acetate anions. The activity strongly depends on the ligand concentration. The optimum ligand/Pd ratio is 1.0; without ligand, no catalytic activity is observed and a black precipitate was formed, while an excess of ligand inhibits the reaction. For instance, with ligand/Pd = 2.0, the activity decreased to 0.6 kg copolymer per gram Pd per hour.

By analogy with the hydrocarboxylation reactions, we suggest that the copolymerization involves initial olefin insertion into a palladium(II) hydride bond. The cationic palladium(II) hydride, $[LPdH\{dpppr-s\}]^+$ (L = H_2O, NCMe, anion or monomer), is formed in situ via successive reduction of $[L_2Pd\{dpppr-s\}]^{2+}$ by CO and water to Pd^0 and oxidative addition of the Brønsted acid. Carbon monoxide and ethene are inserted in an alternating manner, and finally, the chain growth is terminated by hydrolysis of

Table 6
The alternating copolymerization of ethene and carbon monoxide

Run[a]	Ligand	Ligand	Brønsted Acid	(mmol)	kg Polymer/ g Pd · h	Mol. weight (kg/mol)[f]
6/1[b,c]	–	0.0	HOTs	(30.0)	0	–
6/2	dpppr-s	1.0	HOTs	(10.0)	3.58	6.1
6/3	dpppr-s	1.5	HOTs	(10.0)	1.56	6.5
6/4	dpppr-s	2.0	HOTs	(10.0)	0.56	6.1
6/5	dpppr-s	1.0	CF_3COOH	(10.0)	3.87	6.9
6/6	dpppr-s	1.0	H_3PO_4	(10.0)	3.40	n.d.
6/7[d]	dpppr-s	1.0	CH_3COOH	(10.0)	2.25	n.d.
6/8	dpppr-s	1.0	HI	(10.0)	0	–
6/9	dpppr-s	1.0	HOTs	(1.0)	4.03	6.6
6/10[b]	dpppr-s	1.0	HOTs	(0.2)	3.44	7.7
6/11[b]	dpppr-s	1.0	–	(0.0)	2.83	6.5
6/12[b,e]	dpppr-s	1.0	Buffer, pH = 6.8		0	–

[a]Reaction conditions: 0.020 mmol [Pd{OTs}$_2${NCMe}$_2$], ligand and Brønsted acid in water, 141.9 g of total reaction mixture ([Pd] = 0.14 mmol/l), 0.20 mol ethene, 40 bar constant total pressure, reaction temperature: 90°C, reaction time: 60 min., stirring speed: 1000 rpm.
[b]Formation of metallic palladium during the reaction.
[c]Reaction time: 120 min.
[d]Pd(OAc)$_2$ was used instead of [Pd{OTs}$_2${NCMe}$_2$].
[e]KH_2PO_4/Na_2HPO_4 buffer of pH = 6.8 (10 mmol PO_4^{3-}) was used.
[f]Average molecular weight determined by quantitative ^{13}C-NMR analysis, n.d. = not determined.

the palladium acyl bond which regenerates the active hydride species.

Quantitative ^{13}C-NMR of the copolymer samples showed, that the copolymer chains con-
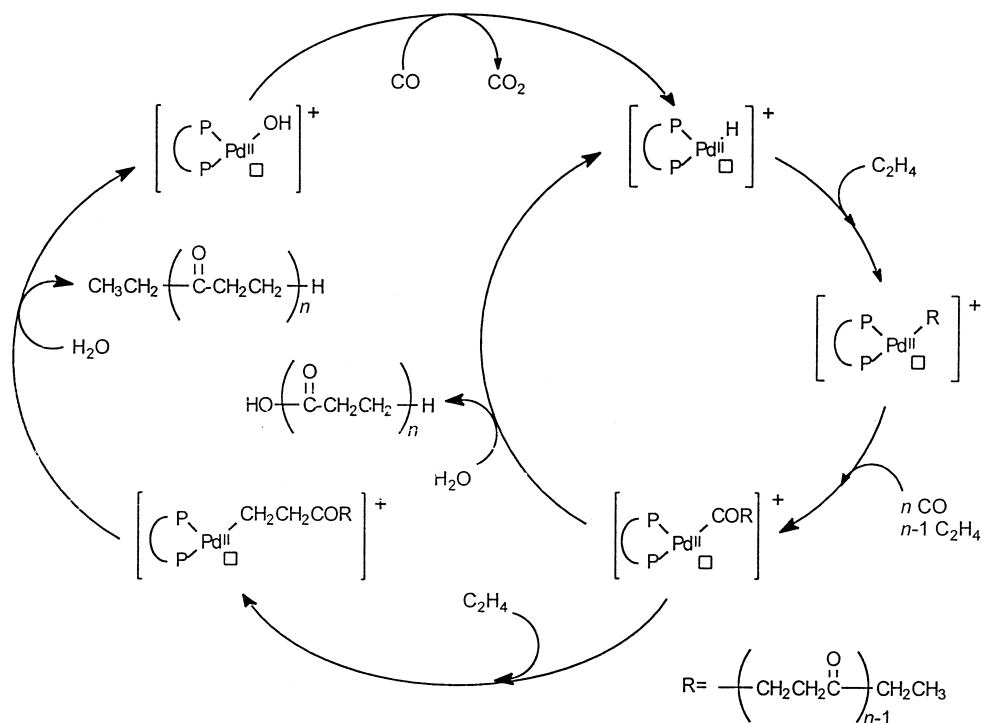
Scheme 5. Proposed mechanism for the Pd/dpppr-s-catalyzed alternating copolymerization of ethene and carbon monoxide [21].

tain approximately 85% keto-end groups and 15% acid-end groups. The formation of extra keto-end groups was previously observed in organic media, especially when some water or hydrogen gas was added to the reaction mixture [17] and it can be explained by the occurrence of two different termination reactions. Besides the 'normal' hydrolysis of a palladium acyl bond, hydrolysis of a palladium alkyl bond occurs, which results in an extra keto-end group and a palladium hydroxo compound (see Scheme 5). In the latter case, the cationic palladium hydride is regenerated by reduction with carbon monoxide.

The copolymerization of CO and propene proceeds considerably slower. The copolymers were obtained as a colorless oil which was separated from the aqueous catalyst solution after adding CH_2Cl_2. An activity of 0.37 kg of copolymer per gram Pd per hour was reached at 90°C which is about 10 times slower than for ethene.

5. Conclusions

The two systems described above, Pd/tppts and Pd/dpppr-s, represent two of the most active palladium-based aqueous phase catalysts. Although the selectivity in the hydrocarboxylation of propene and 1-octene is rather low, this disadvantage might be overcome by tuning the electronic and steric properties of the water-soluble ligand. The presence of an extra α-methyl group on the olefin, as in isobutene, leads to the exclusive formation of the linear isomer. A cyclic olefin, cyclopentene, also underwent highly selective hydrocarboxylation.

The rapid alternating copolymerization of CO and olefins in the aqueous phase is a new environmentally friendly method for the synthesis of polyketones. The possibility of using water as a solvent in this reaction also opens perspectives for the synthesis of new materials with new properties, for instance, when olefins with amphiphilic functions are applied.

Acknowledgements

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