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Carbon monoxide–ethene alternating copolymerization catalyzed by $[PdCl_2(dppf)]$ in H_2O–HCOOH [dppf = 1,1′-bis(diphenylphosphino)ferrocene]

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ABSTRACT

The alternating copolymerization of carbon monoxide with ethene is efficiently accomplished using $[PdCl_2(dppf)]$ as catalyst precursor in H_2O–HCOOH as a solvent. At 90 °C, under 4.5 MPa of total pressure with the monomers in the ratio 1/1, the productivity passes through a maximum of 18,100 gPK(gPd h)$^{-1}$, when the concentration of H_2O is 50 mol.%, in which case the limiting viscosity number of the polyketone is 0.51 dL g^{-1}. A much higher LVN is obtainable at a lower temperature. A satisfactory balance between productivity and LVN is achievable under higher pressure (10,100 gPK(gPd h)$^{-1}$, LVN = 6.5 dL g^{-1} under 9.0 MPa, CO/ethene = 1/1, at 45 °C, H_2O 40 mol.%). The influence of the operative conditions on productivity and LVN is discussed. The kinetics under different pressure of CO, keeping constant that of ethene, and the kinetics under constant total pressure at different CO/ethene ratios show that the copolymerization rates are virtually constant with time within 1 h reaction. The PK presents only keto-end groups ($-COCH_2CH_3$) and catalysis occurs with the concomitant evolution of CO_2. NMR evidences show that the chloride-precursor is transformed, through the interaction of H_2O with CO on the metal center, into a Pd-hydride species that starts the catalysis. A catalytic cycle is proposed.

1. Introduction

Palladium(II)–phosphine complexes are efficient catalysts for the carbonylation of olefins. When used in an alkanol as a solvent, a wide spectrum of products can be obtained ranging from esters to high molecular weight polyketones (PKs) [1–4]. Particularly active are *cis*-coordinated diphosphine "cationic" complexes in which the cationic charge of the metal center is balanced by weakly coordinating anions [5–9]. For the synthesis of PKs, they are normally used in MeOH as a solvent, though with Pd(II) complexes of water soluble diphosphine the copolymerization has been efficiently performed in water [10–12]. In MeOH, the corresponding neutral complexes, in which the cationic charge is balanced by coordinating anions such as chloride, are inactive [5], but they turn into highly active ones when used in a mixture of H_2O and an organic acid, such as HCOOH or CH_3COOH [13–18]. Not only, but the use of this solvent allows for the achievement of PKs of higher molecular weight. Thus, for example, with $[Pd(H_2O)_2(dppf)](TsO)_2$ (dppf = 1,1′-bis(diphenylphosphino)ferrocene) in MeOH, low molecular weight PKs are formed together with cooligomers and other products of even lower molecular weight, such as methyl propanoate, dimethyl succinate, methyl 4-oxohexanoate and dimethyl 4-oxoheptanoate [19]. Instead, with the corresponding chloride in H_2O–CH_3COOH, PKs of moderate molecular weight are formed in a higher yield and in the absence of any lower product [15].

Before this study, we and others patented some results on the CO–ethene copolymerization catalyzed by $[PdCl_2(dppf)]$ in H_2O–HCOOH as a reaction medium [20]. Hereafter, we present the results of a full investigation.

2. Experimental

2.1. Reagents

Carbon monoxide and ethene were purchased from SIAD Company ('research grade', purity >99.9%). Formic acid, acetonitrile, dppf, 1,1,1,3,3,3-hexafluoroisopropanol (99%), CD_2Cl_2, CD_3Cl were Aldrich products; palladium(II) chloride was purchased from Chimet S.p.A. The complexes $[PdCl_2(PhCN)_2]$ and $[PdCl_2(dppf)]$ were prepared as reported in literature [21,22].

2.2. Equipment

The catalyst precursor was weighed on a Sartorious Micro balance (precision 0.001 mg). The gas-chromatographic analysis phase was performed on a Hewlett Packard Model 5890, Series II chromatograph; a HP1, 30 m × 0.35 μm × 0.53 μm column was used for the analysis of the liquid phase of the copolymerization medium

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(detector: FID; carrier gas: N_2, 0.2 mL/min; oven: 50 °C (2 min) to 200 °C at 15 °C/min); for the gas phase a 18 ft × 1/8 SS Silica Gel, 60/80 packed column was used (detector: TCD; carrier gas: helium, 30 mL/min; oven: 40 °C (2 min) to 100 °C at 15 °C/min).

All the NMR spectra were recorded on a Bruker Avance 300 spectrometer. The ^1H NMR and ^{13}C NMR spectra of the PK were recorded in 1,1,1,3,3,3-hexafluoroisopropanol/$CDCl_3$ (10/1) using the Inverse ^1H-Gated Decoupling Technique. The ^{31}P NMR spectra were recorded in CD_2Cl_2.

2.3. *Carbon monoxide–ethene copolymerization*

The CO–ethene copolymerization was carried out in a Hastelloy C autoclave of *ca.* 250 mL provided with a four-blade self-aspirating turbine. Solvent and catalyst were contained in a *ca.* 150 mL Pyrex bottle, placed inside the autoclave, so as to avoid contamination due to possible corrosion of the internal surface of the autoclave.

The monomers were supplied to the autoclave in the ratio 1/1 from a gas reservoir connected to the autoclave through a constant pressure regulator.

In a typical experiment, 0.70 mg of [$PdCl_2$(dppf)] (9.5×10^{-4} mmol) were added to 80 mL of solvent (HCOOH–H_2O, HCOOH = 50 mol.%) contained in the bottle placed in the autoclave. The autoclave was washed by pressurizing with a 1/1 mixture of CO–C_2H_4 (*ca.* 0.5 MPa) and then depressurizing to atmospheric pressure at room temperature with stirring (this cycle was repeated 5 times). The autoclave was then pressurized with 0.5 MPa of the gas mixture and then heated to 90 °C in *ca.* 10 min without stirring. The pressure was then adjusted to the desired value (typically 4.5 MPa total pressure, CO/ethene = 1/1) and, while stirring, maintained constant throughout the experiment (1 h, stirring rate 700 rpm) by continuously supplying the monomers from the reservoir. The kinetics was followed by monitoring the weight drop in the reservoir with time. At the end of the experiment, the autoclave was quickly cooled and carefully depressurized. The PK slurry was filtered, washed with water and acetone and dried under vacuum at 70 °C.

The dried polymer was weighted and the productivity was calculated as gPK(gPd h)$^{-1}$.

In the liquid phase, analyzed by CG, no propanoic acid or other low molecular weight products were found.

The CO_2 evolution during the reaction was monitored by sampling the gas phase of the reactor with a micro-syringe; the gas was then analyzed by GC.

2.4. *Solubility measurements*

The monomers solubility in the solvent of reaction was measured as follows. A known volume of solvent (V_s = 80 mL) was charged into the autoclave used for the copolymerization reaction and heated to the 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 (M) and pressurized to a desired value (P_M) by supplying the monomer from a tank reservoir of known volume (V_r, 88 mL) maintained at constant temperature (T). The initial pressure in the reservoir (P_i) was adjusted at $P_i > P_M$. The liquid was then vigorously stirred till the pressure of the reservoir dropped to a constant final value, P_f. The moles of M absorbed are $n_{M,\text{abs}} = V_r(P_i - P_f)(z_M\text{RT})^{-1}$ and the molar fraction of M in the solvent is $X_M = n_{M,\text{abs}}(n_{M,\text{abs}} + n_{\text{solvent}})^{-1}$.

Henry's law constant H_M (MPa) has been calculated as $H_M = P_M X_M^{-1}$ for $P_M \to 0$.

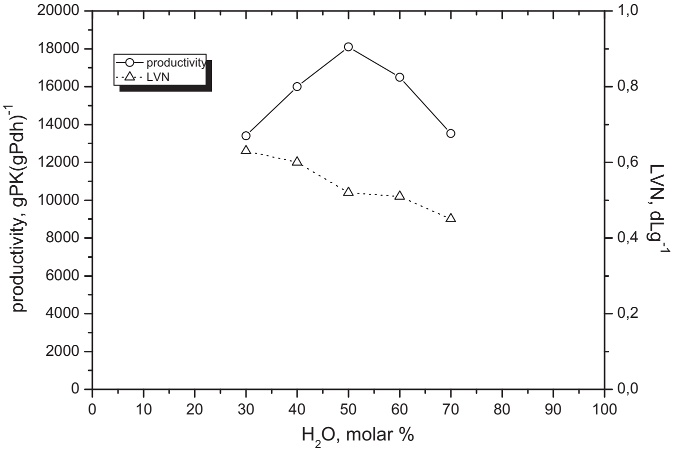

Fig. 1. Influence of the H_2O concentration on the productivity and on the LVN. Run conditions: [$PdCl_2$(dppf)] = 0.70 mg (9.5×10^{-4} mmol); T = 90 °C, P = 4.5 MPa (CO/ethene = 1/1), V = 80 mL (H_2O + HCOOH); reaction time = 1 h.

2.5. *Limiting viscosity number measurement and viscosity-average molecular weight calculation*

The LVN of a dilute *m*-cresol solution of a PK was determined by using the Huggins relationship between the viscosity number and the polymer concentration by extrapolation to zero concentration [23]. The viscosity was measured by using a Cannon–Fenske type capillary viscosimeter, thermostated at 25 °C. The average molecular weight of the polyketone was calculated from the LVN using the following Mark–Houwink equation [24]:

$$[\eta]_{m-\text{cresol},25^\circ C} = 1.01 \times 10^{-4} \bar{M}_v^{0.85}$$

3. Results and discussion

3.1. *General aspects*

[$PdCl_2$(dppf)] is highly active in the alternating CO–ethene copolymerization when used in a mixture of H_2O and HCOOH. The activity strongly depends on the composition of the reaction medium. The highest productivity is achieved when the reaction medium is in the ratio H_2O/HCOOH = 1/1 (mol/mol) (18,100 gPK(gPd h)$^{-1}$ under the conditions of Fig. 1, LVN in the range of 0.45–0.63 dL g^{-1}, $\overline{M}_v = 19,625–29,156$ g mol^{-1}). There is not formation of low molecular weight products that instead are formed when the corresponding cationic catalyst precursor is used in MeOH [19].

The trend of the productivity shown in Fig. 1 has been observed also for other catalytic systems such as [PdX_2(P–P)] (P–P = dppp, X = AcO, Cl; dppf, dapp, X = Cl) (dppp = 1,3-bis(diphenylphosphino)propane), dapp = 1,3-bis(di(2-methoxyphenyl)phosphino)propane in H_2O–CH_3COOH [13–17] and also for the CO–ethene–propene terpolymerization catalyzed by [$PdCl_2$(dppf)] in H_2O–HCOOH [18]. Reasonable explanations for the influence of the solvent composition on the productivity have been already reported [13–18]. They can be summarized as follows. The high polarity of the reaction medium favors the displacement of the coordinating anion, so to ease the coordination of the monomers to the metal center as it occurs in the analogous "cationic" precursors which present easily available coordination sites. Labile coordination of water may stabilize three-coordinated species which may form during the catalysis and have the tendency to dimerize in order to achieve the preferred four-coordination of Pd(II). In general, dimeric species are less active and may lead to decomposition to inactive Pd metal [6]. On the other hand,