Carbon monoxide–ethylene copolymerization catalyzed by a Pd(OAc)$_2$/dppp/formic acid system [dppp = 1,3-bis(diphenylphosphino)propane]

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Abstract

Polyketones are obtained by the copolymerization of carbon monoxide and ethylene in the presence of a palladium catalyst formed in situ from Pd(OAc)$_2$, dppp and formic acid in methanol which acted as a solvent. The productivity (g polymer/g Pd* h) is significantly influenced by the concentration of formic acid. Using the ratio Pd/dppp/HCOOH = 1/1/3000 at 90 °C and 45 atm, a productivity of 7500 h^{-1} is obtained. It is suggested that the efficiency of HCOOH as a promoter is due to its capability to act as a source of Pd-hydride species, which initiates the catalytic cycle.
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1. Introduction

Polyketones obtained by perfectly alternated carbon monoxide–olefin copolymerization [1–6] are of considerable interest because they exhibit an interesting overall set of physical and chemical properties and, in particular, have established their utility as thermoplastics in the production of shaped objects [4,7,8].

The copolymerization requires the use of a catalyst. The catalytic system formed in situ from Pd(OAc)$_2$, dppp, and *p*-toluenesulfonic acid (TsOH) has been found to be highly efficient in methanol [5,6]. It has been pointed out that the anion, in this case TsO$^-$, that balances the charge of the metal complex has to be the conjugate base of a strong acid and that the anion has to be weakly coordinating so that the reacting monomers can easily be activated by coordination to the central metal ion [5,6,9–12]. Using a catalyst of composition Pd/dppp/TsOH = 1/1/2, a productivity of 6200 h^{-1} (g of polyketone/g Pd h) has been obtained at 90 °C and under 40 atm (CO/C$_2$H$_4$ = 1/1) [5]. Subsequently, it has been found that TsOH and H$_2$O have a promoting effect. As a matter of fact, under the conditions reported above, but in the presence of an excess of TsOH (TsOH/Pd = 10/1) and 800 ppm of H$_2$O, a significantly higher productivity can be achieved (8000 h^{-1}) [9]. It has been suggested that the promoting effect of TsOH and H$_2$O is due to their possibility to favour the formation of a Pd-hydride species involved in the initial step of the catalytic cycle [9]. Here we report that a highly efficient catalyst can be formed using relatively weak formic acid in place of TsOH.

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2. Results and discussion

2.1. Effect of the run conditions on the productivity

The copolymerization has been carried out using a palladium catalyst formed in situ from $Pd(OAc)_2$, dppp (Pd/dppp = 1/1 molar ratio) and HCOOH as acid promoter in methanol which acted as a solvent. Preliminary experiments have shown that the catalytic system is efficient when an excess of acid is employed. Fig. 1 shows the amount of polymer obtained versus the catalyst concentration under the conditions reported. The amount of polymer obtained increases linearly with the catalyst concentration up to [Pd] = 2×10^{-4} mol/l, above this concentration the increase is less pronounced, suggesting that the reaction is controlled by the rate of dissolution of the gas into the liquid phase. At this concentration, the apparent activation energy, evaluated by Arrhenius plot (see below), is 4 kcal/mol, indicating that the reaction is controlled by gas/liquid diffusion.

The effect of the temperature on the productivity has been studied using the catalyst system Pd/dppp/ HCOOH = 1/1/3000 and at two different concentrations.

Fig. 2, curve A, shows that the productivity increases with the temperature reaching a value of $7500\,h^{-1}$ at $T = 90\,°C$, when [Pd] = 1.1×10^{-4} mol/l. The apparent activation energy of 14 kcal/mol evaluated by the Arrhenius plot (Fig. 3, curve A) is typical for the CO-ethylene copolymerization reactions [12].

At higher concentration of catalyst, i.e. [Pd] = 2×10^{-3} mol/l (Fig. 3, curve B), the apparent activation energy is about 4 kcal/mol, typical of a diffusion-controlled reaction.

The productivity increases with the total pressure reaching $11000\,h^{-1}$ at 60 atm, as shown in Fig. 4.

2.2. Effect of HCOOH on the productivity

Fig. 5 shows that the productivity significantly increases with the increase in the concentration of HCOOH. In the absence of HCOOH, or at low acid concentration, the catalyst is poorly active. Above HCOOH/Pd = 1000/1, the catalyst activity
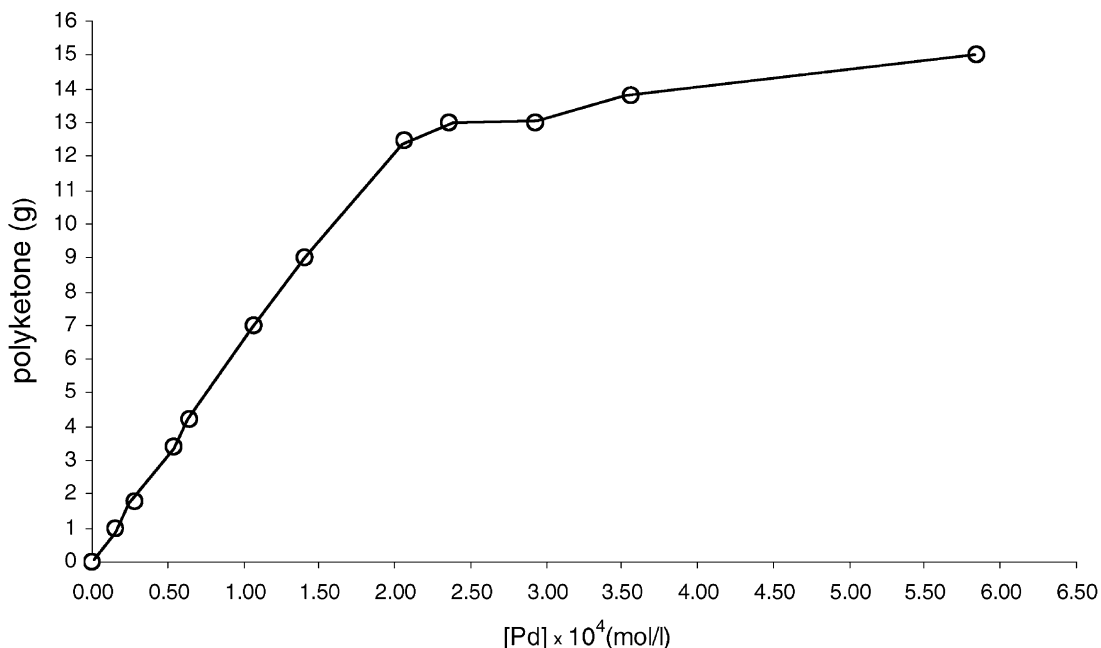

Fig. 1. Catalytic activity as a function of catalyst concentration. Run conditions: Pd/dppp/HCOOH = 1/1/3000; H_2O (initially present in the solvent) = 500 ppm; reaction volume = 80 ml; solvent = MeOH; P_{tot} = 45 atm (CO/C_2H_4 = 1/1, at the working temperature); $T = 90\,°C$; reaction time = 1 h; stirrer speed = 700 rpm.
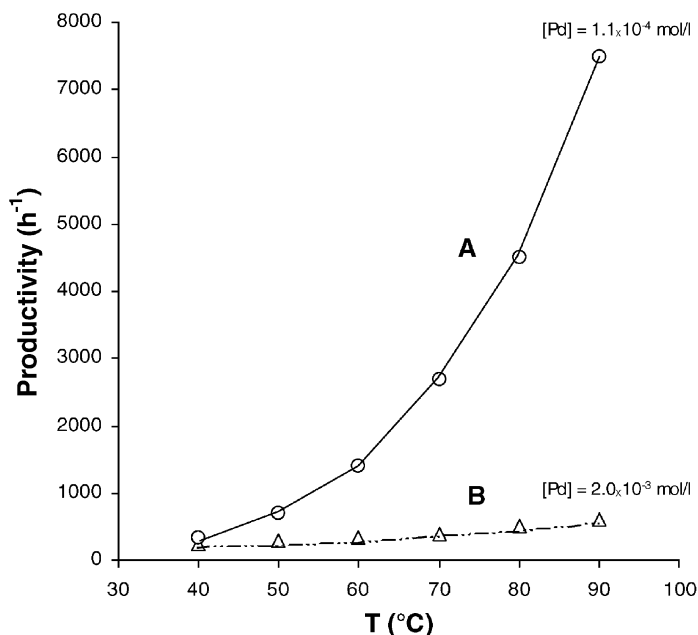
Fig. 2. Effect of temperature on the productivity at two different catalyst concentrations. Run conditions: $Pd(OAc)_2 = 0.0085$ mmol(A); 0.16 mmol (B); Pd/dppp/HCOOH = 1/1/3000; H_2O (initially present in the solvent) = 500 ppm; reaction volume = 80 ml; solvent = MeOH; $P_{tot} = 45$ atm ($CO/C_2H_4 = 1/1$, at the working temperature); reaction time = 1 h; stirrer speed = 700 rpm.

significantly increases to a plateau of $7500\,h^{-1}$ when HCOOH/Pd = 3000/1.

The promoting effect of the acid addition may have several origins. For instance, the acid can increase the concentration of Pd-hydride species by the reactivation of Pd(0) complexes, which inevitably form in the reducing reaction medium [13–16]:

$$Pd(0) + H^+ \rightleftharpoons [Pd-H]^+ \qquad (1)$$

In addition, HCOOH can generate Pd-hydride species [15,17] as schematized below:

$$[Pd-OAc]^+ + HCOOH$$
$$\overset{-AcOH}{\rightleftharpoons} [Pd-O-CO-H]^+ \overset{-CO_2}{\rightleftharpoons} [Pd-H]^+ \qquad (2)$$
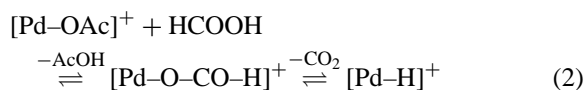
Fig. 6 shows that, at low concentration of acid, TsOH is more efficient than HCOOH; however at higher concentration the latter gives higher activity. In the case of TsOH, the productivity passes through a maximum, probably because there is a competition of the TsO^- anion with the monomers for the coordination to the metal [9]. At high acid concentration the equilibria between the several species present in solution are

shifted towards species having the anion coordinating to the metal. However, when HCOOH is employed in place of TsOH, the Pd-formate species can evolve into an active Pd-hydride species, so the catalyst is active even at high concentration of HCOOH.

In addition, water can react with the metal centre in the presence of CO generating a Pd-hydride species [9,18,19]:

$$Pd^{2+} + CO + H_2O \overset{-H^+}{\rightleftharpoons} [Pd-COOH]^+ \overset{-CO_2}{\rightleftharpoons} [Pd-H]^+ \qquad (3)$$
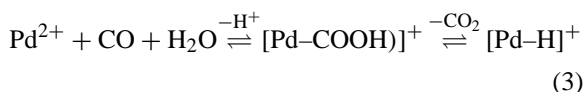
Water is present in the solvent (500 ppm) and forms in higher amounts because of equilibrium (4):

$$HCOOH + CH_3OH \rightleftharpoons HCOOCH_3 + H_2O \qquad (4)$$

In order to differentiate better the role of formic acid in comparison with the role of water in the formation of Pd-hydride species, some reactions have been carried out using acetic acid as promoter instead of formic acid. Acetic acid can increase the amount of water in solution through esterification of the solvent similar to
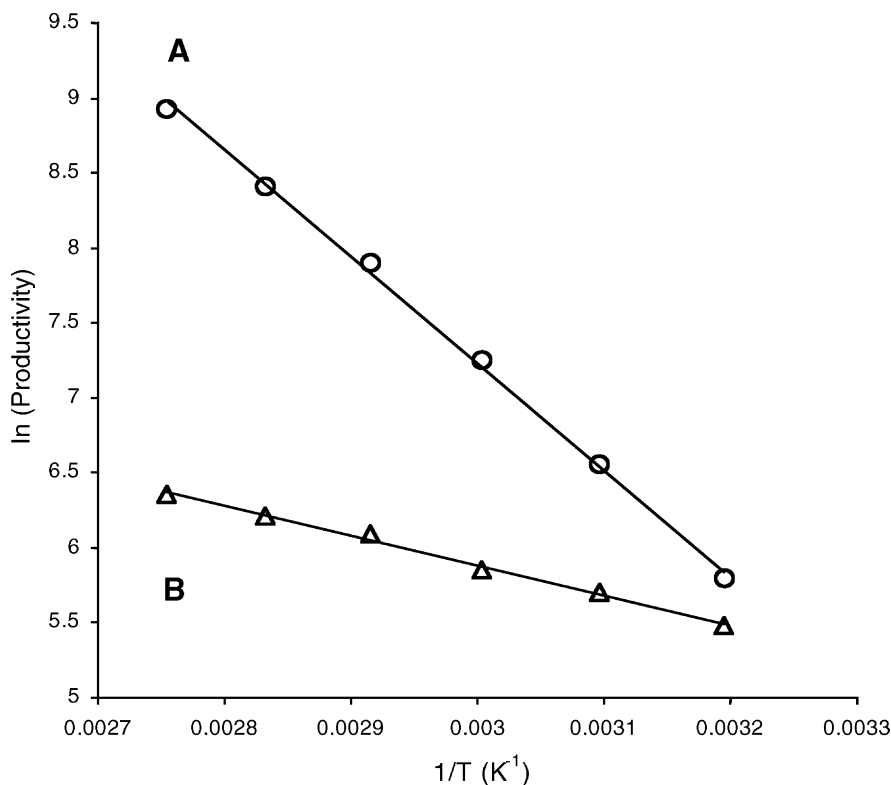
Fig. 3. Arrhenius plots. Run conditions: $Pd(OAc)_2 = 0.0085$ mmol (A), 0.16 mmol (B); Pd/dppp/HCOOH $= 1/1/3000$; H_2O (initially present in the solvent) $= 500$ ppm; reaction volume $= 80$ ml; solvent $=$ MeOH; $P_{tot} = 45$ atm ($CO/C_2H_4 = 1/1$, at the working temperature); reaction time $= 1$ h; stirrer speed $= 700$ rpm.

HCOOH [20,21], but the acetate anion competes with water for the coordination to the metal without producing Pd-hydride species. We found that under the same experimental conditions (Pd/dppp/acid $= 1/1/3000$), acetic acid leads to a low productivity ($100 h^{-1}$), thus suggesting that water plays only a minor role.

2.3. On the mechanism

It is accepted that the copolymer takes origin from the insertion of ethylene into a Pd-hydride bond and/or into a Pd-carbomethoxy bond, which forms in situ by the interaction of CO and methanol on the metal centre [4–9,22–27] (see Scheme 1). On the light of the results obtained, it is plausible to suppose that HCOOH is an efficient promoter because it can act as a Pd-hydride source and that mechanism A plays a major role.

3. Experimental

3.1. Reagents

Methanol was purchased from Baker (purity $>$ 99.5%, 0.05% of water). Formic acid (99%, $d^{20} = 1.22$ g/ml), p-toluenesulfonic acid monohydrate (99%), palladium(II) acetate, and 1,3-bis(diphenyl-phosphine)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 HP 5, 30 m $\times$ 0.35 μm $\times$ 0.53 μm column.
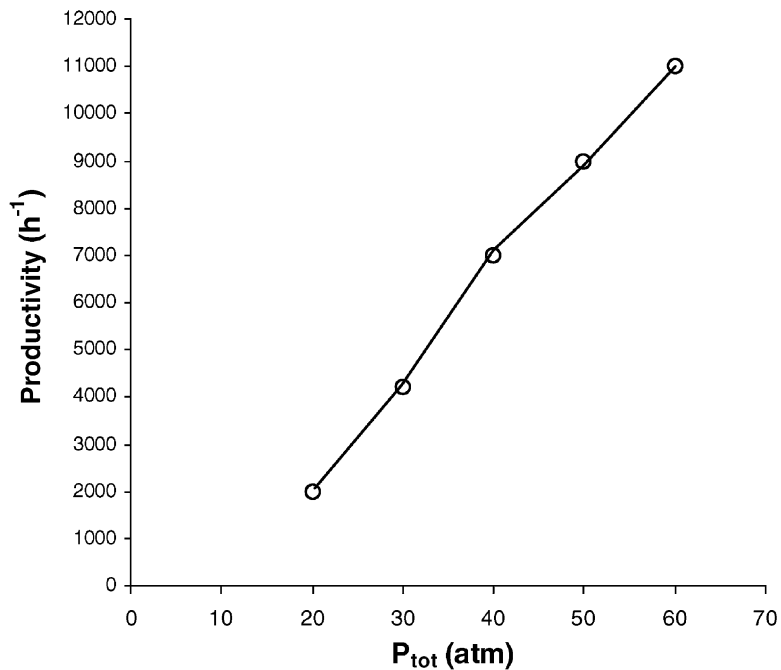
Fig. 4. Effect of total pressure on the productivity. Run conditions: $Pd(OAc)_2$ = 0.0085 mmol; Pd/dppp/HCOOH = 1/1/3000; H_2O (initially present in the solvent) = 500 ppm; reaction volume = 80 ml; solvent = MeOH; T = 90 °C; reaction time = 1 h; stirrer speed = 700 rpm.

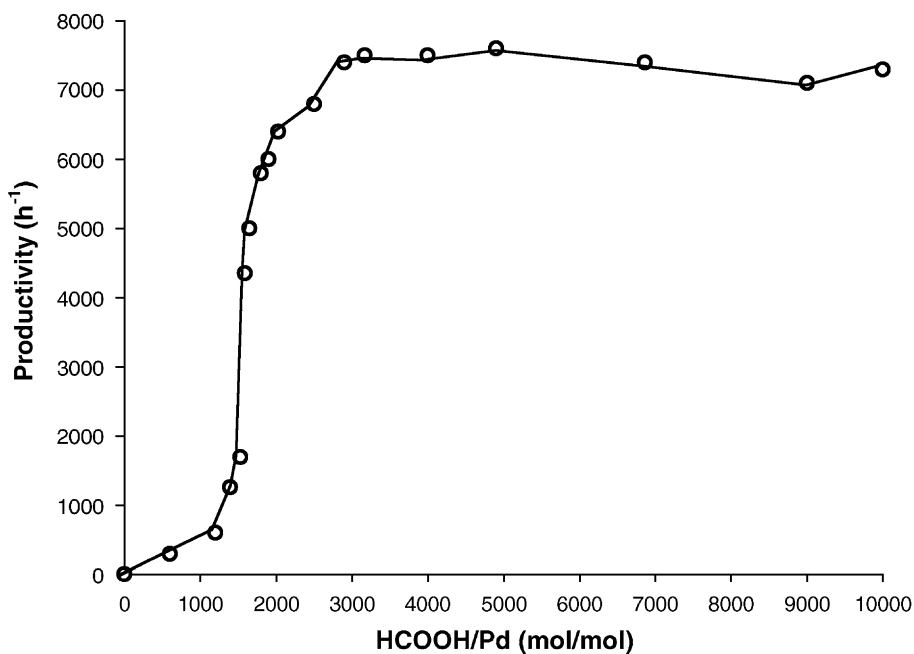Fig. 5. Effect of formic acid concentration on productivity. Run conditions: $Pd(OAc)_2$ = 0.0085 mmol; Pd/dppp = 1/1; H_2O (initially present in the solvent) = 500 ppm; reaction volume = 80 ml; solvent = MeOH; P_{tot} = 45 atm (CO/C_2H_4 = 1/1, at the working temperature); T = 90 °C; reaction time = 1 h; stirrer speed = 700 rpm.

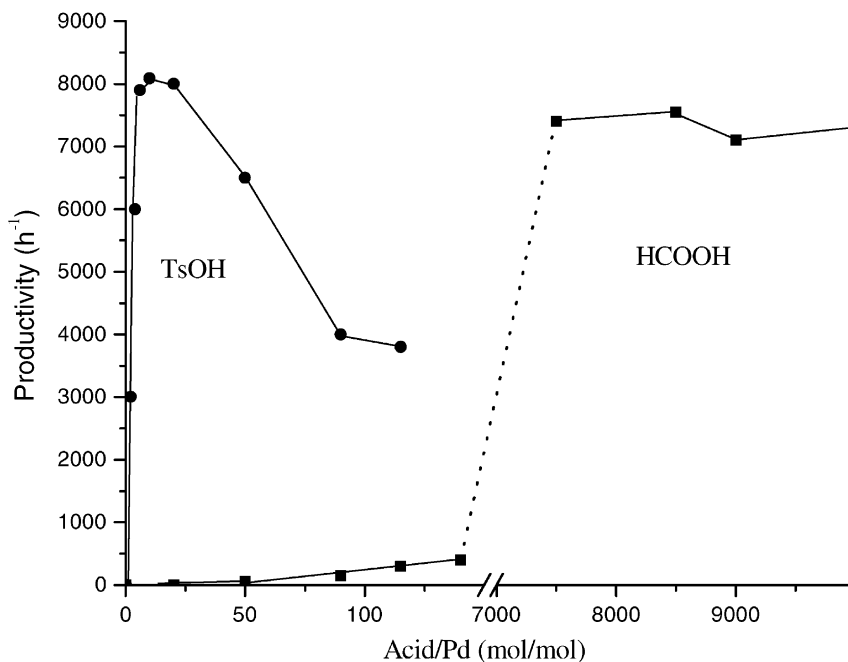Fig. 6. Comparison between the effect of HCOOH and TsOH concentration on productivity. Run conditions: $Pd(OAc)_2 = 0.0085$ mmol; Pd/dppp $= 1/1$; H_2O (initially present in the solvent) $= 500$ ppm; reaction volume $= 80$ ml; solvent $=$ MeOH; $P_{tot} = 45$ atm ($CO/C_2H_4 = 1/1$, at the working temperature); $T = 90\,°C$; reaction time $= 1$ h; stirrer speed $= 700$ rpm.

3.3. Carbon monoxide–ethylene copolymerization

The copolymerization reactions were carried out by using a magnetically driven stainless steel autoclave (AISI 316) of ca. 250 ml provided with a self-aspirating turbine. Solvent and catalyst were added in ca. 150 ml Pyrex bottle placed inside the autoclave, thus preventing contamination by metallic species because of corrosion of the internal surface of the autoclave.

Scheme 1. Pd-hydride catalytic cycle usually proposed in literature.
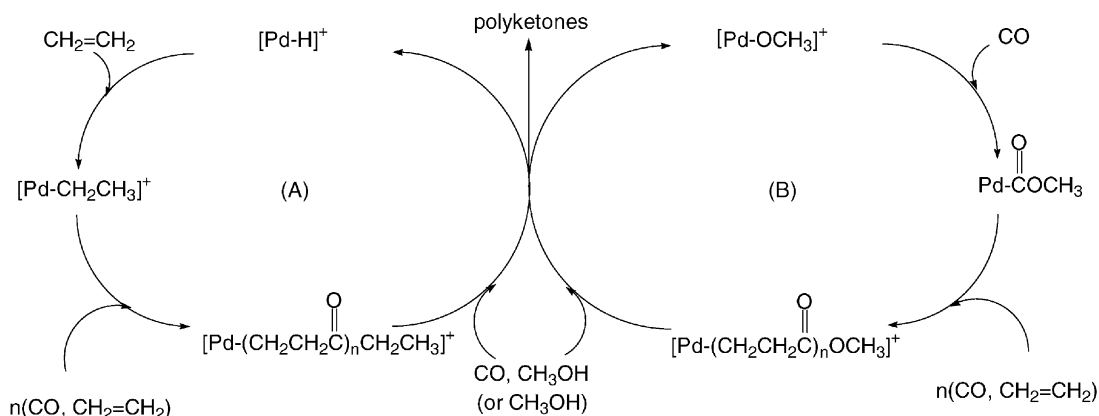
In a typical experiment, 1.90 mg of Pd(AcO)$_2$ (0.0085 mmol), 3.55 mg of dppp and 1 ml of HCOOH (dppp/Pd/HCOOH = 1/1/3000) were dissolved into 79 ml of MeOH. The autoclave was pressurized at room temperature by ca. 10 atm of the two gasses supplied as a 1/1 mixture from a tank reservoir. The autoclave was then heated to 90 °C for ca. 15 min. The pressure was then adjusted to the desired value (typically 45 atm total pressure) and maintained constant throughout the experiment (1 h, stirring rate 700 rpm) by continuously supplying the gasses from the reservoir. At the end of the experiment the autoclave was quickly cooled while releasing the pressure. The product slurry was filtered, washed with MeOH and dried under vacuum at 80 °C.

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