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(1)

Supported palladium metal as heterogeneous catalyst precursor for the methoxycarbonylation of cyclohexene

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Keywords:	The methoxycarbonylation of cyclohexene has been carried out by using Pd metal deposited on a support as
Palladium catalyst	heterogeneous precursors instead of the homogeneous Pd(II) complexes usually proposed in literature. The two
Carbonylation	catalytic systems (homogeneous and heterogeneous) have been compared in methanol in the presence of free
Supported homogeneous catalysis	triphenylphosphine and p-toluenesulfonic acid as promoter. The precursor Pd on Amberlyst IRC 50 led to the

1. Introduction

The alkoxycarbonylation of alkenes, catalyzed by transition-metals, is among the most important processes in the area of homogeneous catalysis [1-3] (reaction 1).

$$R$$
 + CO + R'OH $\xrightarrow{\text{cat.}}$ R $\xrightarrow{}$ O R'

Such reaction is widely used in industry to produce a variety of esters which found application mainly as fragrant components in perfumes, cosmetics, and food essences [4,5], moreover it is also used in many organic syntheses as valuable intermediate products [1-3,6].

As compared to other syntheses of esters, the alkoxycarbonylation of olefins has such important advantages as one-step process, mild reaction conditions, and the use of accessible reagents [1-3]. Furthermore, it is highly atom-efficient which is important for chemical industries interested to the sustainability of the process [7]. Undoubtedly, the Pd (II)-phosphines catalysts appear as the most promising because afford to high activity and selectivity under relatively mild conditions [1-3,8-19]. For instance, in the first step of the Lucite Alpha-process for the production of methyl methacrylate, a very active Pd-diphosphine catalyst is used to catalyze the production of methylpropionate via methoxycarbonylation of ethene [20-25].

With the aim to improve the catalytic activity several authors have studied the influence of the process parameters, the nature of the acid

promoter, the structure of the ligands, the nature of the olefins carbonylated, together with the kinetic and mechanistic aspects of the reaction [26-33]. However, one of the major drawbacks from an industrial point of view of such homogeneous process is the need to recover the catalyst from the reaction mixture [34,35]. An obvious solution to this separation problem could be the use of heterogeneous catalysts, which can be readily recovered by a simple filtration step [36-40]. Among the several approaches proposed, some interesting results have been obtained by immobilizing the homogeneous Pd(II)catalysts on an insoluble support (e.g., silica, alumina [41-44], or polymers [45-57]). However, the synthetic methods usually utilized are complicated leading to partly unknown structures of the Pd(II) species, which are therefore less active but also more unstable (reduction to inactive Pd(0) or Pd metal species).

triphenylphosphine and p-toluenesulfonic acid as promoter. The precursor Pd on Amberlyst IRC 50 led to the best catalytic activity which is comparable to the activity obtained by using the homogeneous Pd(II)-catalyst. The leaching of the metal was negligible and the system has been efficiently recycled at least for three times. A

> In the present paper the authors propose to carry out the methoxycarbonylation of cyclohexene by using Pd metal deposited on a support as heterogeneous catalyst precursor. Such new starting precursor has been compared with an homogeneous ones (for instance with the [Pd(TsO)₂(PPh₃)₂] complex previously studied by the authors [30]) in methanol as solvent and in the presence of phosphines (e.g. triphenylphosphine, PPh₃) and a Bronsted acid (e.g. p-toluenesulfonic acid, TsOH) as a promoter [30,31]. Different heterogeneous pre-catalysts have been readily prepared and tested. Among these the Pd on Amberlyst IRC 50 led to the best catalytic activity, comparable to the homogeneous system [Pd(TsO)₂(PPh₃)₂] [30,31]. The leaching of the

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metal was negligible and the catalyst has been efficiently recycle at least for three times. A reaction mechanism has been also proposed and discussed.

2. Experimental

2.1. Reagents

Methanol, cyclohexene, Palladium(II) acetate, triphenylphosphine (PPh₃), p-toluenesulfonic acid monohydrate (TsOH), Amberlyst IRC 50, Dowex 1-X8, Amberlyst 15, Cellulose MFC (Type 101), Poly(4-vinylpyridine) average $M_w \sim 60,000$, and Poly(4-vinylpyridine-co-styrene) powder were purchased from Sigma-Aldrich; Polyketone was synthesized from CO and ethene (supplied by SIAD Company with 'research grade', purity > 99.9 %) as described in literature [58].

2.2. Equipments

The catalyst precursors were weighted on a Sartorious Micro balance (precision 0.001 mg). Gas-chromatographic (GC) analysis was performed on a Hewlett Packard Model 7890, Series II chromatograph fitted with a HP5, $30 \text{ m} \times 0.35 \text{ mm} \times 0.53 \mu \text{m}$ column (detector: FID; carrier gas: N₂, 0.2 ml/min; oven: 45 °C (3 min) to 250 °C at 15 °C/min).

GC/MS analyses were performed on a MS Agilent apparatus 5975C Model, interfaced with an Agilent chromatograph 7890 A Model equipped with a HP5 column (30 m \times 0.25 mm \times 0.25 µm, oven: 45 °C (3 min) to 250 °C at 15 °C/min).

The ICP-OES (Inductively Coupled Plasma optical emission spectrometry) analyses, to identification and detection of trace metals, were performed by using the PerkinElmer *Optima 7300 DV ICP-OES instrument.

The specific surface area of the powders was measured by Micromeritics Instrument Inc. USA apparatus, ASAP 2010 model.

2.3. Synthesis of Pd-metal supported pre-catalyst

The palladium metal catalyst was successfully supported on the solid showed in Tables 1 and 2 by using a standard wet impregnation method [59,60]. In a typical procedure, 1 g of support was added, at room temperature and under vigorous stirring, to a solution of 65 mg of Pd(OAc)₂ (Pd(II) acetate) in 50 mL of methanol. The Pd(OAc)₂ concentration has been eventually arranged to obtain at the end the desired Pd loading (ca. 3 %, w/w). The suspension was refluxed for 2 h under vigorous stirring to assure a complete reduction of Pd(II) to Pd metal. The solid catalyst was separated by filtration (or by using a permanent magnet when Fe₃O₄ was deposed), washed and dried under vacuum. The amount of Pd-metal deposed on the support was determined through the ICP analysis (confirmed as ca. 3 %, within 1 % of error); the

Table 2

Influence of different heterogeneous catalyst precursors containing magnetite on the methoxycarbonylation of cyclohexene.

entry	Catalyst	Conversion (mol %)	cyclohexane methyl ester detected in solution (mol ^a %)
1	Pd/C (3 %)	83	100
2	Pd/PK, (3 %)	81	100
3	Pd/Amberlyst IRC 50 (3 %)	92	100
4	Pd/Fe ₃ O ₄ , (3 %)	80	8
5	Pd/[C + Fe ₃ O ₄ 5%], (3 %)	69	30
6	Pd/[C + Fe ₃ O ₄ 15%], (3 %)	58	16
7	Pd/[C + Fe ₃ O ₄ 25%], (3 %)	55	12
8	Pd/[PK + Fe ₃ O ₄ 15%], (3 %)	65	25
9	Pd/[Amberlyst IRC50 +	77	31
	Fe ₃ O ₄ 15%), (3 %)		

Run conditions: Pd/Support = 50 mg (Pd 3 %, 0.014 mmol); Pd/PPh₃/ TsOH = 1/50/60; Cyclohexene = 19.74 mmol (2 mL), solvent = MeOH (8.0 mL, 197.75 mmol); T = 120 °C; t = 2 h; $P_{CO} = 50$ atm.

^a [(moles of ester detected)/(moles of cyclohexene converted)]*100.

specific surface area of each solid has measured by using the $\rm N_2$ fisisorption-BET technique.

2.4. Synthesis of magnetic supports

The synthesis of magnetic supports was performed by deposition of Fe_3O_4 nanoparticles on support surface [40] (see Table 2). In a typical procedure, 0.115 g of Fe_3O_4 , suspended in 5 mL of methanol, was added under vigorous stirring to 1 g of support (carbon black or PK) suspended in 20 mL of methanol. The mixture has refluxed for 1 h and then the solid has separated by a permanent magnet, washed with fresh methanol and dried under vacuum. The specific surface area has measured by using the N_2 fisi-sorption-BET technique.

2.5. Experimental setup

All the experiments were carried out in a stainless steel batch reactor of *ca*. 50 mL of capacity, provided with a magnetic stirrer and a temperature control system (\pm 0.5 °C). Carbon monoxide was supplied from a gas reservoir (260 mL) connected to the reactor through a constant pressure regulator.

2.6. Experimental procedure

In a typical experiment, known quantities of the pre-catalyst, PPh_3 and TsOH along with 8 mL of methanol and 2 mL of cyclohexene were charged into the reactor. The reactor was purged twice with carbon monoxide at room temperature with stirring, pressurized with a low CO

Table 1

Influence of different heterogeneous catalyst precursors on the methoxycarbonylation of cyclohexene.

entries	Catalyst	Specific area (m ² /g)	Average porous diameter (nm)	Conversion (mol %)	TOF [mol ester/ (molPd ^a * h ⁻¹)]	Leaching of Pd (w/w %)
1	[Pd(PPh ₃) ₂ (TsO) ₂] ^b	-	-	93	646	100 ^b
2	Pd/Carbon (3 %)	842	6	83	577	6
3	Pd/PK ^c (3 %)	40	20	81	563	5
4	Pd/Cellulose	2	20	82	570	6
5	Pd/Amberlyst IRC 50 (3 %)	2	6	92	649	0.3
6	Pd/Amberlyst 15 (3 %)	40	30	91	643	0.1
7	Pd/Dowex 1-X8 (3 %)	0.3	11	42	292	12

Run conditions: Pd/Support = 50 mg (Pd 3 %, 0.014 mmol); Pd/PPh₃/TsOH = 1/50/60; Cyclohexene = 19.74 mmol (2 mL), solvent = MeOH (8.0 mL, 197.75 mmol); T = 120 °C; t = 2 h; P_{CO} = 50 atm.

^a is the total Pd metal present in the support before the reaction.

^b homogeneous catalyst Pd/PPh₃/TsOH = 1/50/60 (mol/mol) [30,31].

^c PK = poly(1-oxo trimethylene), named polyketone [61,62].

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pressure (ca. 5 atm) and then heated up. At the working temperature the pressure was adjusted to the desired value (typically 50 atm total pressure) and maintained constant throughout the experiment (i.e. 2 h) by continuously supplying the carbon monoxide from the reservoir. At the end of each experiment the reactor was quickly cooled to room temperature and vented. The solid was recovered by filtration, washed and dried under vacuum. To determinate the amount of leaching it has been measured the amount of Pd on the solid before and after the reaction by using the ICP technique (the % of leaching has been expressed as [[(g of Pd in the solid before reaction)-(g of Pd in the solid after reaction)]/(g of Pd in the solid before reaction)]x100. The qualitative and quantitative analysis of the liquid was performed by using the GC-MS and GC technique. The conversion has been expressed as: [(initial moles of cyclohexene - final moles of cyclohexene)/ initial moles of cyclohexene] * 100; In all experiments the material balance has been verify and the selectivity to ester was 100 %

2.7. Recycling experiments

The pre-catalyst was recovered from the reaction solution through a simple filtration. It was thoroughly washed many time with methanol and acetone and then dried under vacuum. The solid was weighted and reused in the next reaction. In this case we prefer to evaluate the catalytic activity in term of TOF (Turnover Frequency: moles of ester/ (moles of Pd*h)) which was calculated by considering that all the amount of metal deposited on the surface was active in the catalysis. This is because during the recycling operations part of the catalyst (usually < 5 %) could be lost. The leaching in the successive reactions was measured through the ICP analysis of the liquid phase. The next reaction was carried out following the same procedures above described (section 2.5).

3. Results and discussion

The methoxycarbonylation of cyclohexene (reaction 2) has been efficiently carried out by using a heterogeneous catalyst precursor, based on Pd metal deposited on an unsolvable support (Tables 1 and 2). Although it was widely reported that such reaction is not catalyzed by Pd metal [1–3,26–33], we found that by adding free PPh₃ and TsOH, similarly to the homogeneous catalytic systems [26–33], it can readily form the active species and lead to the ester in high yield.

3.1. Influence of different supports on the catalytic activity

The Table 1 shows the activity of several Pd_{metal} -supported heterogeneous catalysts which has been compared with the activity obtained by using the homogeneous $[Pd(PPh_3)_2(TsO)_2]/PPh_3/TsOH$ (1/50/60) system, previously studied by some of the authors [30,31].

All the pre-catalysts tested lead to good conversion regardless of porosity and specific surface area of the support. Among these, Pd_{metal} on Carbon (Pd/C), Pd_{metal} on polyketone (Pd/PK) and Pd_{metal} on cellulose (Pd/cell) lead to comparable conversions (81–83 %), whereas Pd_{metal} on ion exchange resins lead to different results (entries 5–7). In particular, Pd_{metal} on Dowex 1-X8 leads to the worse conversion (42 %, entry 5), whereas Pd_{metal} on Amberlyst IRC 50 and Pd_{metal} on Amberlyst 15 lead to the best conversions (92-91 %, entries 5, 6), which are almost comparable to the conversion obtained by using the homogeneous catalyst (93 %, entry 1).

All the heterogeneous catalysts have been readily recovered at the end of reaction by using a simple filtration apparatus. The leaching of the metal measured was very poor when Pd/Amberlyst IRC 50 (3 %) or

Pd/Amberlyst 15 (3 %) has been used (Table 1, entries 5 and 6) whereas it is higher when Pd/Dowex 1-X8 (3 %) is used (entry 7). Moreover, based on our previous work [40], it has been deposited a dosed amount of ferrimagnetic Fe_3O_4 (magnetite) on the surface of some supports in order to allow an easier recovery of the catalyst by using an external magnetic field.

Table 2 shows that the addition of Fe_3O_4 decreases the conversion of cyclohexene (entries 4–9) and that it differs consistently from the amount of cyclohexane methyl ester effectively detected in solution; Unfortunately, at the end of the reaction all the catalysts have lost the initial magnetic properties. By increasing the amount of Fe_3O_4 on the support the cyclohexene conversion slightly change and it further decreases the amount of ester detected in solution (entries 4–6). As in such experiments the material balance is not satisfied (not further by-products were detected), we suppose that both cyclohexene and/or its ester could be chemisorbed on the Fe_3O_4 causing also the lost of its magnetic features. This point was not further investigated because it was not in the aim of the present work. However, on the light of such results we decided to avoid the use of Fe_3O_4 and to optimize the reaction conditions by using the precursor Pd/Amberlyst IRC 50, which leads to the best result.

3.2. Influence of PPh_3 and TsOH on the catalytic activity and on the leaching of palladium

The Fig. 1 shows that, in absence of PPh₃ and at constant acid concentration (for instance TsOH/Pd = 60/1), the reaction is not catalyzed by Pd/Amberlyst IRC 50. However, by increasing the PPh₃/Pd molar ratio the catalyst become active and the conversion passes through a maximum of 92 % when it is *ca*. 50/1.

At PPh₃/Pd lower than *ca*. 45/1, the leaching of Pd measured was less than 5 % of the initial metal deposited on the support. On the other hand, at PPh₃/Pd higher than 45/1 the lost of metal rapidly increases, reaching *ca*. 15 % when PPh₃/Pd is ca. 120/1 (conversion of *ca*. 50 %).

According with the studies on the homogeneous catalysis [26–33], it is plausible that PPh₃ reacts with the Pd_{metal} deposited on the surface of the support forming solvable Pd(0) complexes. Such a complexes are transformed in the active species (probably Pd(II)-H) through reaction with the acid which increases the catalytic activity (see the Fig. 2). However the conversion passes through a maximum because the increase of free PPh₃ concentration stabilizes the inactive Pd(0) species against the active Pd(II)-H ones, causing a decrease of catalytic activity (see the Fig. 1 and reaction mechanism).



Fig. 1. Influence of PPh₃ on the catalytic activity of Pd/Amberlyst IRC 50 (3 %). Run conditions: Pd/Amberlyst IRC 50 = 50 mg (Pd 3 % w/w); Pd/TsOH = 1/ 60 mol/mol; Cyclohexene = 19.74 mmol (2 mL), solvent = MeOH (8.0 mL); T = 120 °C; t = 2 h; P_{CO} = 50 atm. TOF = moles of ester/[(moles of Pd in the solid before reaction)*(reaction time)].



Fig. 2. Influence of TsOH on the catalytic activity of Pd/Amberlyst IRC 50 (3 %).

Run conditions: Pd/Amberlyst IRC 50 = 50 mg (Pd 3 %, w/w); Pd/PPh₃ = 1/ 50 mol/mol; Cyclohexene = 19.74 mmol (2 mL), solvent = MeOH (8.0 mL); T = 120 °C; t = 2 h; P_{CO} = 50 atm. TOF = moles of ester/[(moles of Pd in the solid before reaction)*(reaction time)].

According to this, the Fig. 2 shows that the catalyst is not active without acid and linearly increases by increasing the TsOH concentration (constant PPh₃ concentration, PPh₃/Pd = 50/1).

3.3. Influence of temperature on the catalytic activity of Pd/Amberlyst IRC 50 (3 %)

By increasing the temperature, the conversion passes through a maximum at *ca.* 120 °C (see Fig. 3). At reaction temperatures higher then 120 °C the conversion decreases, suggesting deactivation of the catalyst probably due to decomposition of the active Pd(II) species to form inactive Pd(0) complexes or Pd metal, similarly to what is reported when the homogeneous catalytic system is used [30]. To note that the leaching of metal practically does not change at different temperatures remaining in all the tests below the 3 % w/w.

3.4. Catalyst recycle

The heterogeneous precursor has been recovered at the end of each reaction and recycled (see experimental section). The Fig. 4 shows that



Fig. 3. Influence of temperature on the catalytic activity. Run conditions: Pd/Amberlyst IRC 50 = 50 mg (Pd 3 %, w/w); Pd/PPh₃/TsOH = 1/50/60 (mol/mol); Cyclohexene = 19.74 mmol (2 mL), solvent = MeOH (8.0 mL); T = 120 °C; t = 2 h; $P_{CO} = 50$ atm.

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Fig. 4. Influence of catalyst recycling on the catalytic activity and on the leaching of Pd.

the same precursor can be used at least two times without significant metal losses due to leaching (< 0.2 %). At the third time, however, the catalytic activity decreases whereas the leaching increases up to 6.3 %.

3.5. On the reaction mechanism

The results above discussed suggest that the active species can form in situ by reaction between PPh₃, TsOH and Pd metal, similarly to what is proposed in literature when the reaction is carried out by using the Pd (II) homogeneous catalyst [1–3,26–33]. Consequently, we propose the same reaction mechanism, schematized in the Fig. 5.

According to this, the solvable Pd-hydride species forms in situ from Pd metal deposited on the solid surface and the free CO, PPh_3 and TsOH, present in solution, for instance following the reaction 3 and 4.

$$Pd_{metal} + (4-n)PPh_3 + n CO \rightleftharpoons [Pd(CO)_n(PPh_3)_{4-n}] \text{ with } n=0-4$$
(3)

$$[Pd(CO)(PPh_3)_3] + TsOH \rightleftharpoons [PdH(CO)(PPh_3)_2]^+(TsO)^- + PPh_3$$
(4)

As the Pd(0) and/or Pd(II) complexes formed are solvable in the reaction medium, it is plausible to suppose also that they determinates the leaching observed. As a matter of fact, the Fig. 1 shows that by using a large excess of PPh₃ (PPh₃/Pd higher than 50/1) the leaching increases, but also decreases the conversion according to the fact that under such conditions is favoured the formation of solvable, but inactive, Pd(0) complexes. Moreover the low leaching generally measured in the experiments reported in Table 1, suggests that the reaction occurs faster



Fig. 5. Scheme of the proposed reaction mechanism.



Fig. 6. Influence of reaction time on the catalytic activity and on the leaching of Pd.

Run conditions: cat: Pd/Amberlyst IRC 50 = 50 mg (Pd 3 %, w/w); cat/PPh₃/ pTsOH = 1/50/60 (mol/mol); Cyclohexene (2.0 mL, 19.74 mmol); MeOH = 8.0 mL; T = 120 °C; P_{CO} = 50 atm.

than the diffusion of the solvable Pd(0) (or Pd(II)) species into the bulk and that such species are somehow retained within the solid. It is plausible therefore that the catalysis starts near the surface and, depending by the relative concentration of PPh₃ and TsOH (in particular inside the pores), the solvable Pd-species readily decompose forming Pd metal again (equilibrium 3 moves to the left), which is re-deposited on the surface.

According to this, the Fig. 3 shows that by increasing the temperature (> 110 °C) the conversion decreases suggesting a thermal decomposition of the catalyst with probable formation of Pd_{metal}. However, at each temperatures tested, the leaching of Pd measured was very poor (< 0.12 %), according with the hypothesis that a re-deposition of Pd_{metal} on the surface of the support readily occurs. This is further supported by the finding that the leaching is not influenced by the reaction time (Fig. 6 shows that at 7 h it is very low, < 0.12 %) but only by the PPh₃ and TsOH concentrations (Figs. 1 and 2).

A further influence on the amount of leaching measured should be due to the nature of the support In facts, the Table 1 shows that when a cations exchange support was used the leaching was very poor (entries 5 and 6). As a matter of facts, the carboxylate groups present in the Amberlyst IRC 50 (sulfonate in Amberlyst 15) could interact with the cationic Pd(II) species readily formed in situ. Such interaction could

Table 3

Effect of addition of a pyridine based metal scavenger.

Experiment (entry)	scavenger	catalyst	Conversion (mol %)	TOF (h ⁻¹)
1		^a Pd/IRC 50	92	649
2		Pd/IRC 50 recycled from exp.	89	627
		1		
3	PVPy	Pd/IRC 50	3	21
4	^c PVPy- co-Sty	Pd/IRC 50	5	35
5		Pd/IRC 50 recycled from exp.	n.d.	-
		3		

Run conditions: Pd/Amberlyst IRC 50 (3 %) = 50 mg; Pd/PPh₃/TsOH = 1/50/60; Cyclohexene = 19.74 mmol (2 mL), solvent = MeOH (8.0 mL); T = 120 °C; t = 2 h; P_{CO} = 50 atm.

^a Pd/IRC 50 = Pd/Amberlyst IRC 50 (3 %).

^b PVPy = Poly(4-vinylpyridine) average $M_w \sim 60,000 = 150$ mg.

^c PVPy- co-Sty = Poly(4-vinylpyridine-*co*-styrene) powder = 150 mg.

allow to the metal to remain inside the solid phase avoiding the leaching. It is therefore plausible to suppose that the functional groups of the support act as "heterogeneous" coordinating ligands (Fig. 7, path a) and/or as cations exchanging resin between H^+ and the [Pd(II)]⁺ cationic species which form during the catalytic cycle (Fig. 7, path b).

With the aim to test the homogeneity/heterogeneity of the catalytic system, a metal scavenger has added to the reaction mixture [63–70]. In particular it has been added a polymer containing pyridine ligand (see Table 3) which is referred as effective scavengers for soluble Pd complexes or salts, due to the ability of the pyridine moiety to bind Pd species [68–70].

The Table 3 shows that the addition of such metal scavenger causes a decrease of catalytic activity (entries 3, 4), supporting the hypothesis that the catalysis was due to the formation of solvable Pd-species into the pores. According to this, in the experiment in which the Pd/Amberlist IRC 50 has been recycled (entry 5) the ester has not detected.

4. Conclusions

The methoxycarbonylation of cyclohexene can be efficiently carried out in methanol by using palladium metal deposited over an unsolvable support as catalyst precursor. Although the catalytic activity depends on the PPh₃ and TsOH concentration and on the temperature, the best results both in terms of productivity and leaching have been obtained by using cations exchange supports.

Such heterogeneous system is proposed as a more sustainable catalytic pathway for the alkoxycarbonylation of olefin in comparison to



Fig. 7. Scheme of the possible interactions of the Pd(II) complexes and the functional groups of the support. Path a: coordination to the metal center; Path b: cations exchanging.

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the homogeneous catalysis (comparable results in terms of conversion). This is because at first the catalyst can be readily recovered from the solution through a simple filtration with a leaching of metal < 1 %under optimized conditions, but also because it is stable (Pd metal), it enables to easily weight a low amount of metal (3 % of Pd metal is dispersed into an inert solid medium) and it can be recycled efficiently at least for three time.

CRediT authorship contribution statement

Andrea Vavasori: Conceptualization, Methodology, Data curation, Writing - original draft, Supervision, Writing - review & editing, Sara Bravo: Methodology, Data curation, Francesco Pasinato: Data curation. Nurbolat Kudaibergenov: Writing - review & editing. Luca Pietrobon: Data curation. Lucio Ronchin: Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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