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# Promising polymer-assisted extraction of palladium from supported catalysts in supercritical carbon dioxide

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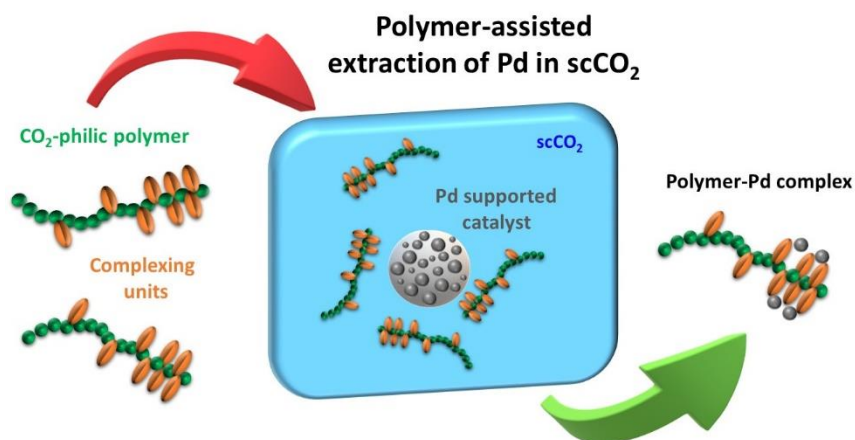
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## Abstract

Precious metals, in particular palladium (Pd), have a wide range of daily applications, from automotive catalysts to fine chemistry production. Nevertheless, these metals are relatively rare and highly expensive, considering their massive industrial utilization. In the last decades, different recycling methods have been explored. Nowadays, the most applied methods, namely pyro- and/or hydrometallurgy, involve energy-intensive processes and/or the generation of large amounts of effluents to be treated. Thus, the development of a more sustainable recycling process of precious metals is highly desirable. In the present work, we introduce a sustainable process based on the use of a green solvent, supercritical CO<sub>2</sub>, operated under mild conditions (P = 25 MPa and T = 40 °C). The extraction process is possible thanks to the addition of CO<sub>2</sub>-soluble complexing polymers bearing pyridine units. The proposed method leads to the extraction of more than 70% of Pd from an aluminosilica-supported catalyst.

## Graphical Abstract



**Keywords:** catalyst; extraction; palladium; polymer; supercritical fluid

**Short title:** Palladium extraction in supercritical carbon dioxide

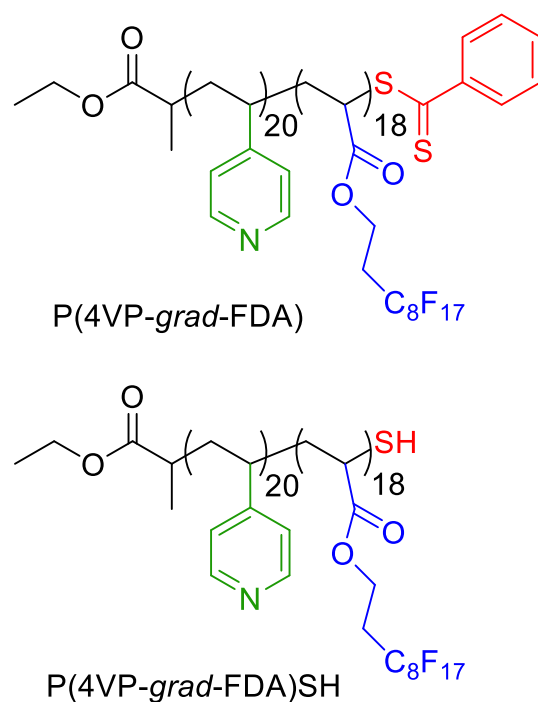
## 1. Introduction

Precious metals play a key role in our daily lives. Owing to their unique properties, these elements find applications in a wide variety of industries and products, from petrochemistry to automotive applications. The yearly demand of precious metals is increasing due to industrial applications. In particular, the demand for palladium (Pd) has risen from 242 tons in 2010 to over 305 tons in 2018[1]. Despite the constantly growing demand of Pd over the past years, there is a supply deficit as mine production is not able to meet these demands, resulting in an increase in prices. For these reasons, alternative sources of the precious metal are necessary[2]. To date, the recovery of precious metals from spent catalysts has been performed with different techniques[3]. Pyrometallurgical and hydrometallurgical technologies, vacuum carbon-thermal reduction and high temperature incineration methods are the most commonly used techniques for the recycling of precious or critical metals and are thoroughly described in various reviews[2–4]. The aforementioned procedures require high temperatures (over 1000 °C)[5] or generate large amounts of effluents (usually strong acidic or basic solutions)[6]. This results in energy-intensive and environmentally hazardous processes.

Recently, different methods have been studied to recover precious metals from waste materials, involving technologies based on ionic liquids[7], polyphosphonates[8], ion exchange resins[9] or solvent extraction[10]. Thus, this research area is very active in the development of novel greener and safer methods to implement an improved and sustainable process to recover and recycle such precious metals.

An alternative procedure is the utilization of supercritical CO<sub>2</sub> (scCO<sub>2</sub>) as extraction medium. scCO<sub>2</sub> is considered a green solvent, characterized by its high availability and tunable solvent power. In addition, the supercritical domain can be achieved at mild conditions ( $T_c = 31$  °C,  $P_c = 7.38$  MPa), making scCO<sub>2</sub> an environmentally friendly and inexpensive medium for industrial applications. Being a nonpolar solvent, scCO<sub>2</sub> is not effective by itself to perform metal extraction in the absence of proper additives that are able to interact with the precious metal. In the literature, dithiocarbamates, beta-diketones, dithizone, and perfluorocarboxylic acids have been tested as complexing additives[11–15]. Thus, our group has recently proposed the development of a polymeric extractant soluble in scCO<sub>2</sub>, constituted by CO<sub>2</sub>-philic fragments (1,1,2,2-tetrahydroperfluorodecylacrylate, FDA) and complexing units (diphenylphosphinostyrene, DPPS)[16]. This first report showed the ability of this polymer to extract up to 50% of precious metal from an alumina-supported Pd catalyst.

In the present article, we present a novel extraction formulation to remove Pd from an aluminosilica-supported catalyst through the use of new CO<sub>2</sub>-soluble complexing polymers: poly(4-vinyl pyridine-*grad*-1,1,2,2-tetrahydroperfluorodecylacrylate) P(4VP-*grad*-FDA) and a thiol-terminated poly(4-vinyl pyridine-*grad*-1,1,2,2-tetrahydroperfluorodecylacrylate) P(4VP-*grad*-FDA)SH (Figure 1). These polymers contain pyridine complexing units able to interact with Pd species and CO<sub>2</sub>-philic FDA monomer units to confer solubility in scCO<sub>2</sub>. Although some non-fluorinated polymers such as siloxane-based[17,18] or vinyl alkanoate-based[19,20] polymers are soluble in scCO<sub>2</sub>, fluorinated FDA-based copolymers were chosen for this study because they usually exhibit exceptional solubility in dense CO<sub>2</sub> with low sensitivity to molecular weight and nature of the chain-ends[21–23]. In contrast, non-fluorinated polymers are mostly soluble at low molecular weights and are sensitive to the nature of the chain-ends[24,25]. Moreover, we have focused on gradient copolymers instead of block copolymers because the latter usually require higher CO<sub>2</sub> pressures to be solubilized in dense CO<sub>2</sub>[26]. This method is proposed as an alternative and innovative process to extract Pd from supported catalysts by using a green method, avoiding the use of high temperatures and the generation of hazardous effluents.

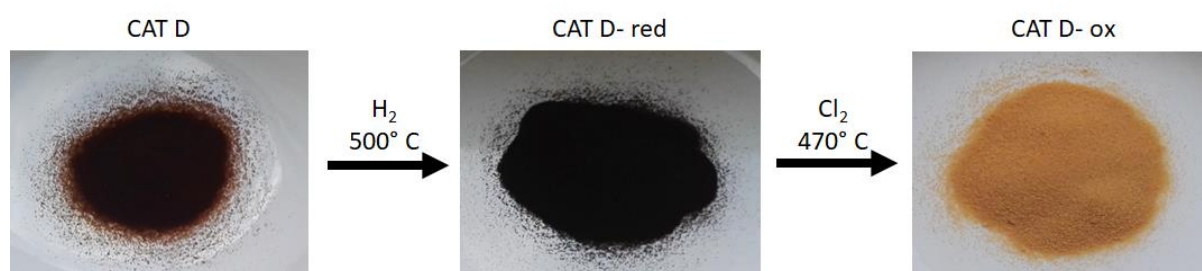


**Figure 1.** Structures of the gradient copolymers P(4VP-grad-FDA) and P(4VP-grad-FDA)SH used for the extractions of Pd from the supported catalysts.

## 2. Experimental Section

The catalysts used for these studies have been provided by Heraeus Deutschland GmbH & Co. KG: pristine catalyst D (CAT D), catalyst D after reduction over 4h under H<sub>2</sub> atmosphere at 500 °C (CAT D-red), and catalyst D after reduction and subsequent oxidation over 4h under Cl<sub>2</sub> atmosphere at 470 °C (CAT D-ox) (Figure 2). CAT D is a pristine, industrial aluminosilica-supported catalyst used for the initial extraction experiments. This catalyst is similar to the common spent catalysts that Pd would normally be recycled from in terms of material and catalyst type, and therefore would help to reflect realistically on the performance of the extraction in industrial settings. The characterizations of the catalysts are reported in the supporting information (inductively coupled plasma optical emission spectrometry (ICP-OES), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX), nitrogen adsorption-desorption isotherms (BET)). Carbon dioxide (CO<sub>2</sub>, SFE 5.2, Air Liquide, 99.9%) was used as received. The polymer synthesis has been performed following the procedures shown in the Supporting Information (SI), adapted from a previous work[27]. The polymer characterization is also shown in the SI. The procedure for the extraction was as follows (Figure S1): catalyst (≈ 200 mg) and P(4VP-grad-FDA) (≈ 220 mg) were added in the 35 mL stainless-steel extraction cell (Top Industrie, France), which was then tightly closed. In the case of CAT D-ox, 0.02 mL of DIPEA (N,N-diisopropylethylamine) were added to buffer the eventual release of HCl during the extraction (chlorine in Na<sub>2</sub>PdCl<sub>4</sub>). The ISCO pump was stabilized at P = 27 MPa and T = 35 °C. Afterwards, the extraction cell was filled with CO<sub>2</sub> until 25 MPa at 40 °C were reached in the cell. The extraction was performed under magnetic stirring at 100 rpm for one hour at 25 MPa and 40 °C (batch conditions), and then the cell was flushed with

≈160 ml of CO<sub>2</sub> (26 MPa and 35°C in ISCO pump) at a flow rate of approximately 0.6-1.2 mL/min. Afterwards, the extraction cell was opened and the catalyst was recovered (Sample A). The cell was cleaned with acetone, which was subsequently collected and then evaporated (Sample B). Samples A and B were analysed by ICP-OES to determine the amount of precious metal extracted: Extraction conversion (%) = E (%) =  $[1 - (\text{mass of Pd}_{\text{sampleA}} + \text{mass of Pd}_{\text{sampleB}}) / (\text{mass of Pd}_{\text{initial catalyst}})] \times 100$ . As detailed in Table S1, the calculated extraction conversion (E %) is related to the total mass of Pd (samples A and B) left in the cell after extraction, therefore there is no further correction to apply. The errors bars  $\Delta E/E$  (%) on extraction conversion have been calculated considering the following accuracies: accuracy of weighing balance of  $\pm 1$  mg, ICP-OES measurements are accurate within  $\pm 6$  %.



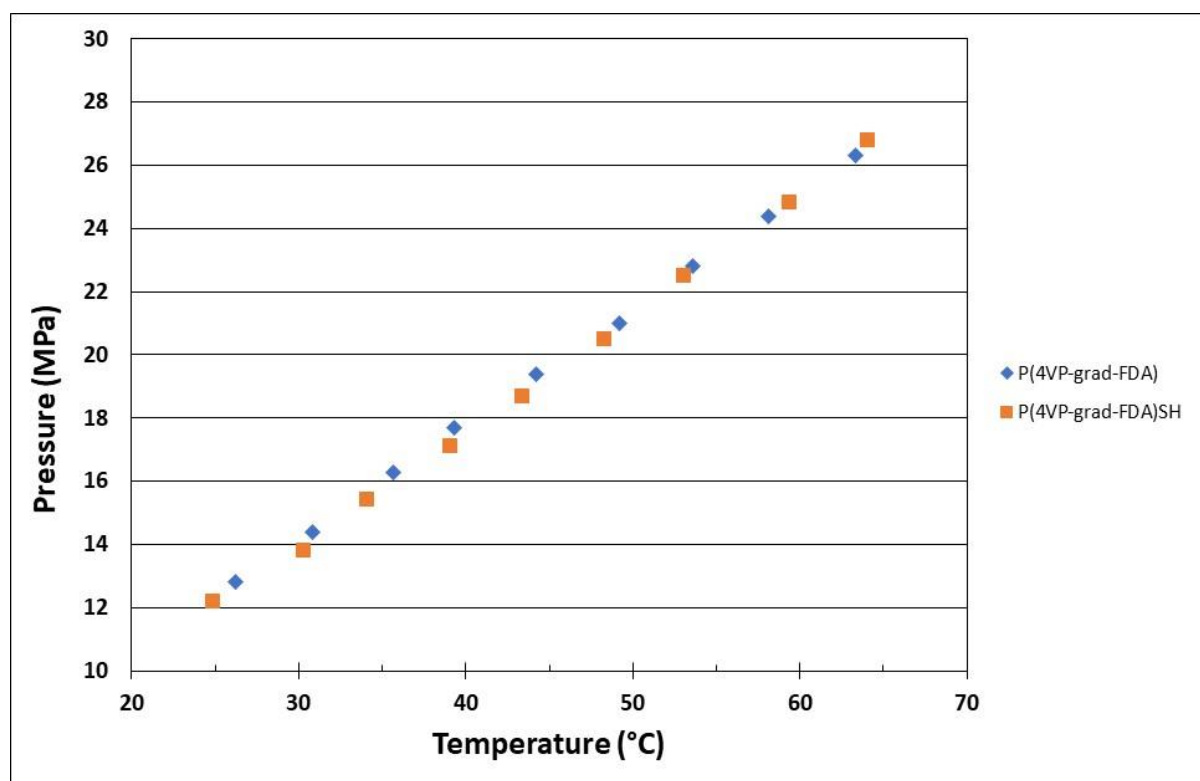
**Figure 2.** Pictures of the Pd supported catalysts CAT D, CAT D-red and CAT D-ox studied in this work.

### 3. Results and discussion

The catalysts used for these extraction experiments (CAT D, CAT D-red and CAT D-ox) were characterized through different analytical techniques to determine the concentration of the supported Pd (ICP-OES) and its oxidation state (XPS), the porosity of the catalyst (BET), the spatial distribution of the metal in the catalysts (SEM-EDX), and the metal particle size (TEM) (see the Supporting Information). All the catalysts have 2 wt% of Pd (Tables S2-S3) and they are supported on an aluminosilica support (Table S4). For all the studied catalysts, the metal is present mainly on the surface of the support (Figures S2-S3); nonetheless, traces of metal could also be detected in the inner part of the material (Figure S4). The average pore size of the aluminosilica support is 21-22 nm, determined by nitrogen adsorption-desorption isotherms (BET) (Figures S5-S7, Table S5). Previous studies[26,28] have shown that amphiphilic fluorinated polymers are prone to form micelles in scCO<sub>2</sub>. In particular, polymers weighing between 10 and 20 kg/mol form micelles, with diameters in the order of 10 nm. Thus, the pore diameter of the catalyst support is larger than the diameter of the micelles, allowing a proper interaction of the polymer with the precious metal even in the inner parts of the supported catalyst. All the supported catalysts used in this study have similar physical properties in terms of pore size and metal distribution. The main differences between the catalysts are the Pd oxidation states and the nature of the Pd species on the support, as well as the Pd particle size. CAT D contains palladium oxide PdO (100%) (Figure S8), with an average particle size of 2.7 nm (Figure S9). CAT D-red contains Pd<sup>0</sup> (79%) and PdO (21%) (Figure S10), characterized by an increase of the average particle size, up to 3.3 nm (Figure S11). Finally, CAT D-ox contains mainly Na<sub>2</sub>PdCl<sub>4</sub> (85%) with a minor amount of PdO (15%) (Figures S12-S13, Table S4). Consistently, in the case of CAT D-ox, TEM analysis showed the presence of a smaller amount of Pd particles at nanoscale dimensions, corresponding to the remaining PdO (Figure S14). Indeed, due to the low contrast of the Na<sub>2</sub>PdCl<sub>4</sub> in TEM[29], it was not possible to see this salt which was adsorbed on the catalyst.

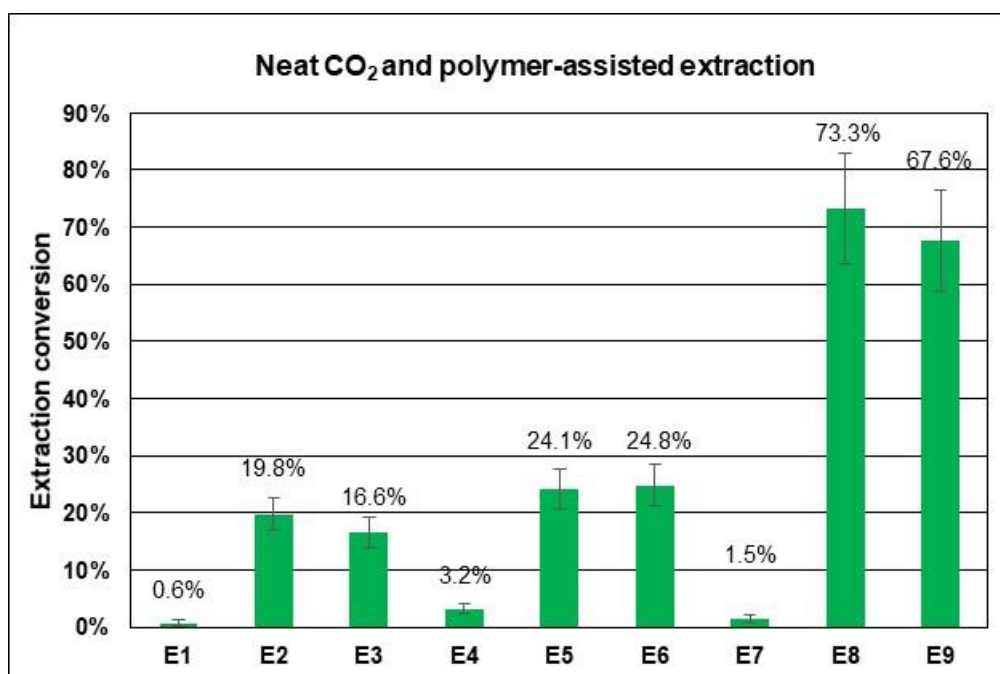
The variation of the Pd oxidation state and the nature of the Pd species in the different catalysts are due to a pretreatment applied for the purpose of this work (Figure 2). The aim of modifying the oxidation state and the nature of the Pd species is to evaluate the efficiency of the extraction process on different Pd species ( $\text{Pd(II)O}$ ,  $\text{Pd}^0$ , and  $\text{Na}_2\text{Pd(II)Cl}_4$ ) while keeping the same catalyst support (aluminosilicate) and metal distribution.

The polymers were synthesized by controlled radical polymerization using the reversible addition-fragmentation chain transfer (RAFT) technique [27]. The Alfrey and Price Q and e values of 4VP and FDA are available in the literature:  $Q_{4VP}=2.47$  and  $e_{4VP}=0.84$ [30],  $Q_{FDA}=0.44$  and  $e_{FDA}=0.45$ [31]. From these Q and e values, the reactivity ratios could be estimated by using the classical Alfrey and Price equations[30]:  $r_{4VP}=4.05$  and  $r_{FDA}=0.21$ . Thus, 4VP is preferably introduced during copolymerization with FDA and there is a composition drift within the polymer chains (the beginning of the polymer chain is enriched in 4VP units), leading to a gradient copolymer structure for P(4VP-*grad*-FDA) (Figure S15) and P(4VP-*grad*-FDA)SH (Figure S16). The cloud point curves of the copolymers were determined in dense  $\text{CO}_2$  (Figure 3, Table S6). The copolymers were shown to be soluble in mild conditions of pressure, lower than 30 MPa in the full range of temperatures from 25 to 65 °C, as expected from previous works[26–28]. Notably, the aminolyzed copolymer P(4VP-*grad*-FDA)SH (Figure S16) has very similar cloud point pressures as its parent copolymer, indicating the negligible effect of the chain-end on the cloud point curve thanks to the high solubility of this kind of FDA-based fluorinated copolymer in dense  $\text{CO}_2$ .



**Figure 3.** Cloud point curves of P(4VP-*grad*-FDA) (diamond) and P(4VP-*grad*-FDA)SH (square) in dense  $\text{CO}_2$  (at a polymer concentration of *ca.* 1 wt% of polymer relative to  $\text{CO}_2$ ).

The extraction procedure involves the use of mild supercritical operating conditions, at  $P = 25$  MPa and  $T = 40$  °C, similar to those currently used for the decaffeination in  $scCO_2$  at industrial scale[32], making the metal extraction process potentially readily available for upscaling and commercial applications. Indeed, Manjare *et al.*[33] have reported that the relatively higher investment requirement in supercritical fluid extraction (SFE) processes is well compensated by several benefits, such as the low cost of  $CO_2$ , shorter batch times, and negligible energy requirement of solvent recovery from the extract. In addition, there is no cost of pollution treatment since there is practically no effluent generated by SFE plants. In the present work, the conditions of temperature and pressure ( $P = 25$  MPa and  $T = 40$  °C) were chosen above the cloud point curve of the copolymers, ensuring that the copolymers are solubilized in  $scCO_2$  during the extraction process. The goal of the first experiments was to verify that the nonpolar  $scCO_2$  alone is unable to extract Pd. Without polymer, for all the tested catalysts, less than 3% of Pd was removed from the catalyst support (Figure 4) (Table 1, runs E1, E4, E7), confirming the negligible solubility of the Pd species in neat  $scCO_2$  and the requirement of a complexing agent as additive.



**Figure 4.** Extractions of palladium from CAT D (E1, E2, E3), CAT D-red (E4, E5, E6) and CAT D-ox (E7, E8, E9) in the absence of complexing polymer (E1, E4, E7) and in the presence of complexing polymers P(4VP-*grad*-FDA) (E2, E5, E8) and P(4VP-*grad*-FDA)SH (E3, E6, E9) in  $scCO_2$  at  $T = 40$  °C and  $P = 25$  MPa.

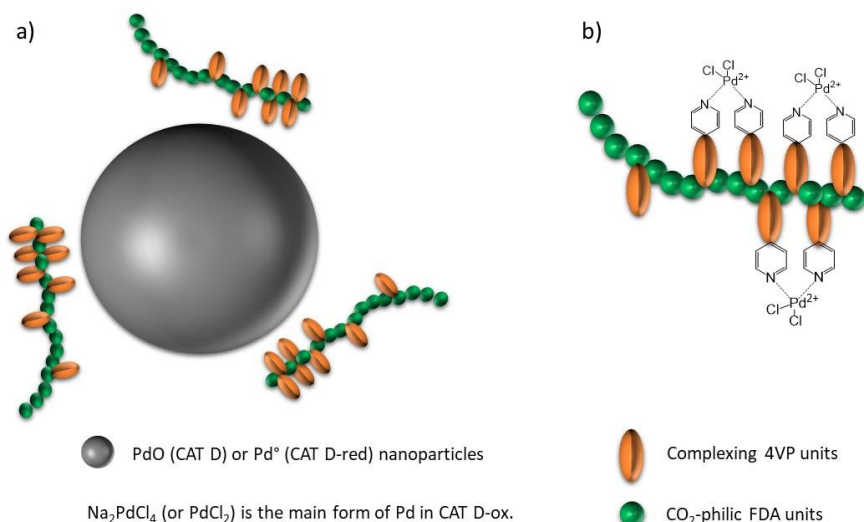
Subsequently, the extractions of Pd from the supported catalysts have been performed in  $scCO_2$  in the presence of P(4VP-*grad*-FDA) as complexing agent (Figure 1). As can be seen from the extraction tests with  $CO_2$  alone (E1, E4, E7), the polymer is fundamental for the metal extraction. This was expected as supercritical  $CO_2$  is a nonpolar system and consequently there is almost no chemical interaction between the metal and  $CO_2$ . Therefore, it was decided to prepare a  $CO_2$ -philic polymer bearing several pyridine units, well-known to interact and form complexes with metals like Pd and Pt[34–36].

The first polymer-assisted extraction experiments were performed at 25 MPa and 40 °C on CAT D, CAT D-red and CAT D-ox with the polymer P(4VP-*grad*-FDA) (Table 1, runs E2, E5, E8). This complexing

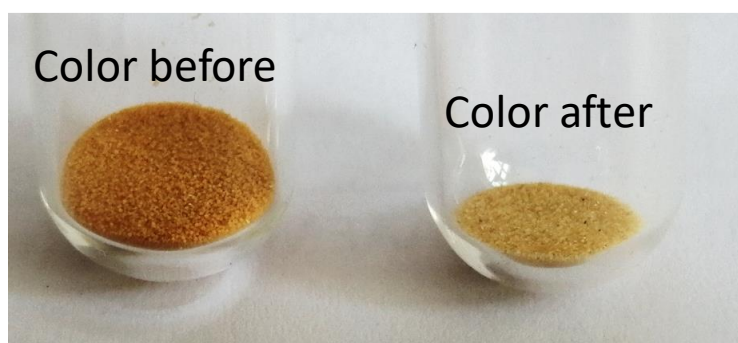


polymer ( $M_n$  11830 g/mol) contains an average of 20 units of pyridine, allowing for good complexing ability, and 18 FDA units (Figure S15), necessary to obtain a polymer that is soluble in  $scCO_2$  under mild conditions of pressure. The extraction on CAT D showed low efficiency (19.8%) (Figure 4 and Table 1, run E2), due to the strong interaction between PdO and the aluminosilica support as well as poor reactivity of such Pd derivatives toward organic ligands. With the reduced catalyst (Cat D-red) containing Pd<sup>0</sup>, the extraction was only slightly improved (24.1%) (Figure 4, Table 1, run E5). The low efficiency of this polymer to interact with and remove the metal from the supported catalyst can be explained by the low affinity of the pyridine units as ligand in relation with the Pd<sup>0</sup> nanoparticles. As shown in the Supporting Information, for both PdO and Pd<sup>0</sup> loaded catalysts, the Pd nanoparticles on the aluminosilica support have a diameter in the order of 3 nm. Presumably, the polar pyridine units favor the adsorption of the amphiphilic gradient copolymer on the surface of the Pd nanoparticles. Thus, thanks to the  $CO_2$ -solubility of the polymer due to the FDA units, the PdO and Pd<sup>0</sup> nanoparticles can be dispersed in  $scCO_2$ , with the polymer playing the role of a steric stabilizer (Figure 5a). It is important to notice the influence of the complexing polymer on the extraction process: in fact, the extraction of Pd increases from 0.6% and 3.2% (respectively for CAT D and CAT D-red without polymer) to 19.8% and 24.1% in the presence of the amphiphilic  $CO_2$ -soluble polymer P(4VP-*grad*-FDA) (Figure 4).

Finally, the polymer-assisted extraction procedure with the polymer P(4VP-*grad*-FDA) has been tested with the catalyst CAT D-ox, which contains mainly Na<sub>2</sub>PdCl<sub>4</sub> (Figure 4 and Table 1, run E8). The extraction experiment led to a remarkable efficiency, allowing for the removal of 73.3% of the Pd absorbed on the catalyst. The successful Pd extraction can actually be observed visually by a change of color of the supported catalyst (Figure 6). As illustrated in Figure 2, the colored Pd species give the reddish-brown color to CAT D-ox (the aluminosilica support is white). In Figure 6, the reddish-brown color of CAT D-ox decreased after extraction because of the removal of the colored Pd species from the catalyst support. There was no significant volume nor mass change of the supported catalyst after extraction because there is only 2 wt% Pd on the catalyst support. The improved result obtained with CAT D-ox can be explained by the enhanced reactivity of the Na<sub>2</sub>PdCl<sub>4</sub> halogenated species with the pyridine ligand in comparison with the oxide (PdO) (CAT D) or metallic (Pd<sup>0</sup>) (CAT D-red) species. Indeed, halogenated Pd derivatives are commonly used as precursors in organometallic chemistry to synthesize novel complexes containing the precious metal[37–41]. Thus, the complexation of the precious metal by the polymer ligand sites, combined with the  $CO_2$ -solubility of the polymer, makes the solubilization of the Pd/polymer supramolecular species and their transportation in the  $scCO_2$  medium possible, resulting in a promising polymer-assisted extraction of Pd from the aluminosilica-support of the catalyst (Figure 5b).



**Figure 5.** (a) Steric stabilization of the PdO or Pd° metallic nanoparticles by the polymer P(4VP-*grad*-FDA) in scCO<sub>2</sub> for the catalysts CAT D and CAT D-red; (b) formation of CO<sub>2</sub>-soluble supramolecular complexes Pd/P(4VP-*grad*-FDA) for the catalyst CAT D-ox.



**Figure 6.** Change of color of the supported catalyst CAT D-ox after supercritical CO<sub>2</sub> extraction of Pd assisted by the copolymer P(4VP-*grad*-FDA) at 40 °C and 25 MPa: a) color of CAT D-ox before extraction; b) color CAT D-ox after extraction.

After these first experiments, the polymer P(4VP-*grad*-FDA) has been modified by aminolysis in order to obtain P(4VP-*grad*-FDA)SH (Figure 1), bearing a thiol end-group, thus providing a good Pd-complexing unit to the polymer. This functionalization was performed to improve the metal extraction. Indeed, the sulphur-based molecules are well-known ligands for Pd species and are commonly used as complexing agents for metal recovery[42–44].

**Table 1.** Polymer-assisted extractions of Pd from aluminosilica-supported catalysts in supercritical CO<sub>2</sub> at T = 40 °C and P = 25 MPa<sup>[a]</sup>.

Run	Supported catalyst	Polymer	Complexing group	Polymer/Pd molar ratio	Complexing group/Pd molar ratio	Extracted Pd from the support of the catalyst (%) <sup>[b]</sup>
E1	CAT D	None	None	0	0	0.6 ± 0.6
E2		P(4VP <sub>18</sub> - <i>grad</i> -FDA <sub>20</sub> )	4VP	0.56	11.1	19.8 ± 2.9
E3		P(4VP <sub>18</sub> - <i>grad</i> -FDA <sub>20</sub> )SH	4VP SH	0.50	10.5	16.6 ± 2.6
E4	CAT D-red	None	none	0	0	3.2 ± 0.9
E5		P(4VP <sub>18</sub> - <i>grad</i> -FDA <sub>20</sub> )	4VP	0.55	11.1	24.1 ± 3.5
E6		P(4VP <sub>18</sub> - <i>grad</i> -FDA <sub>20</sub> )SH	4VP SH	0.50	10.6	24.8 ± 3.6
E7	CAT D-ox	None	none	0	0	1.5 ± 0.7
E8		P(4VP <sub>18</sub> - <i>grad</i> -FDA <sub>20</sub> )	4VP	0.56	11.2	73.3 ± 9.6
E9		P(4VP <sub>18</sub> - <i>grad</i> -FDA <sub>20</sub> )SH	4VP SH	0.51	10.7	67.6 ± 8.9

<sup>[a]</sup> General conditions: m<sub>catalyst</sub> = 200 mg, m<sub>polymer</sub> = 220 mg, m<sub>CO<sub>2</sub>,batch step</sub> = 35 g, m<sub>CO<sub>2</sub>,flushing step</sub> = 145 g.

<sup>[b]</sup> Determined by inductively coupled plasma - optical emission spectrometry (ICP-OES).

Unexpectedly, the extractions were not improved by the use of the thiol-terminated P(4VP-*grad*-FDA)SH polymer as complexing agent (Figure 4, Table 1, runs E3, E6, E9). Therefore, the thiol group of P(4VP-*grad*-FDA)SH does not bring benefits to the steric stabilization of PdO (CAT D) and Pd<sup>0</sup> (CAT D-red) nanoparticles, nor in the supramolecular complexation of Na<sub>2</sub>PdCl<sub>4</sub> (CAT D-ox). In all cases, the contribution of the single thiol group is not significant enough compared to the 20 4VP units of the polymer chain.

The extraction conversion of 73% obtained for CAT D-ox with P(4VP-*grad*-FDA) copolymer represents a promising polymer-assisted extraction of palladium from supported catalysts in scCO<sub>2</sub>. Indeed, even

though the experimental conditions for the extraction have not been optimized yet, high extraction conversions have already been accomplished. Tan *et al.*[20] have reported high extraction conversions (>70%) of Ni<sup>2+</sup>, Co<sup>2+</sup> and Cu<sup>2+</sup> by supercritical CO<sub>2</sub> extraction assisted by oligo(vinyl acetate) bearing a bipyridine moiety, similar to those reported by our group[45] for cobalt extraction using a fluorinated polymer bearing phosphonic acid moieties; nevertheless, the support of the metal was not aluminosilica but filter paper[20] or cotton fabric,[45] respectively. In previous works of Pd extraction from supported catalysts in scCO<sub>2</sub>, even higher extraction conversions (up to 99%) were obtained, but under optimized conditions and using hazardous chemicals like HNO<sub>3</sub>[43,46,47]. Compared to these earlier studies, the Pd extraction conversion of 73% obtained in the present work, without optimization and without generating hazardous waste streams, appears to be a very promising result. The amount of polymer used in run E8, leading to 73 % extraction conversion, is 0.259 g of P(4VP-*grad*-FDA) for 0.208 g of supported catalyst CAT D-ox. This weight ratio of polymer/catalyst of 1.2 is quite low compared to the amount of solvent used in hydrometallurgy where the liquid/solid ratio for leaching is typically in the range of 10[48]. The extraction methods such as pyrometallurgical processes and various hydrometallurgical and leaching methods[49] have been reviewed for the recovery of precious metals from supported catalysts[50,51]. Among them, alternative methods such as supercritical fluids extraction (scCO<sub>2</sub> and supercritical water), ionic liquid-assisted extraction[52], ultrasound-assisted pre-treatments for bioleaching[53] and microwave-assisted leaching[44] are considered to also have good potential to leach precious metals such as Pd. Nevertheless, there are still some challenges to achieving environment-friendly and sustainable recycling for precious metals with a high recovery rate. Thus, future technologies for precious metals recycling need to be more efficient and to have less environmental impact, lower cost, and higher recovery rate. In this context, polymer-assisted extraction in supercritical CO<sub>2</sub> could be a way to avoid the use of low molecular weight, hazardous leaching agents.

As a conclusion, a promising method for the extraction of Pd from aluminosilica-supported catalysts in scCO<sub>2</sub> under mild conditions (P = 25 MPa and T = 40 °C) has been demonstrated by using a CO<sub>2</sub>-soluble complexing polymer containing pyridine units P(4VP-*grad*-FDA). In this work, over 70% of the Pd precious metal has been removed from an aluminosilica support, by an environmentally friendly and non-destructive process, avoiding high energy demanding procedures or generation of polluting effluents. These studies will be pursued to further improve this extraction process, for instance through the use of different CO<sub>2</sub>-soluble complexing polymers (including non-fluorinated ones) and testing different extraction parameters (time, pressure, temperature). This method opens up the route for the development of a sustainable technology able to extract precious metals from porous supports, the first step of a recycling process with an increasing importance in modern industrial activities and in the emerging circular economy. Further steps will include the separation of Pd from the polymer-Pd mixture and the investigation of various methods for Pd recovery after its extraction by scCO<sub>2</sub>. In addition, a comparative life cycle assessment (LCA)[54–56] between a conventional process and the process reported herein is envisioned to evaluate the technico-economical feasibility and the sustainability of the proposed polymer-assisted extraction process of precious metals in supercritical CO<sub>2</sub> compared to other traditional methods.

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