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Extraction of palladium from alumina-supported catalyst in supercritical CO_2 using functional fluorinated polymers

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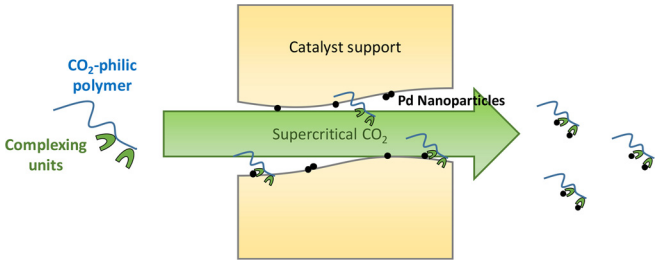
GRAPHICAL ABSTRACT



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ABSTRACT

The use of functional CO_2-philic polymers in supercritical carbon dioxide ($scCO_2$) for a greener method of extracting Pd from spent catalysts has been investigated. Three fluorinated polymers bearing complexing units (a thiol-terminated poly(1,1,2,2-tetrahydroperfluorodecyl acrylate) homopolymer PFDA-SH, a poly(1,1,2,2-tetrahydroperfluorodecyl acrylate-*co*-diphenylphosphinostyrene) gradient copolymer P(FDA-*co*-DPPS), and a thiol-terminated gradient copolymer P(FDA-*co*-DPPS)-SH) were synthesized and successfully used to extract palladium from commercial Pd/Al_2O_3 supported catalysts (beads and pellets with 0.5 wt.% and 5 wt.% Pd loading, respectively). These non-destructive extractions were carried out in $scCO_2$ under mild conditions (40 °C and 25 MPa). Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis on the Pd/Al_2O_3 catalysts before and after extraction confirmed the removal of palladium from the catalytic supports. Up to 40% of palladium was extracted from the commercial supported catalysts with full recovery of the original alumina support.

1. Introduction

Heterogeneous catalysis has been extensively used for decades, especially in the petroleum and automobile industries. These important catalytic processes often require platinum group metals (platinum, palladium, and rhodium), which are typically dispersed in a porous supporting material, such as ceramics [1]. The high demand of these metals over the last decades has led to a shortage in supply as well as to a rise in cost, rendering these processes expensive to employ [2]. Nonetheless, these catalytic processes are necessary and there are no viable replacements for these catalysts to date. Spent catalytic converters are therefore recycled in order to recover and reuse these precious metals [3–5]. To date, the most widely used methods for the recovery or recycling of these noble metals are through pyrometallurgical

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processes or wet-chemical etching [5]. With these processes, the destruction of the catalytic support is inevitable and large quantities of toxic fumes are produced, which require a complex post-treatment process before being released to the environment [6]. The efficiency of these processes is also low, with only approximately 10% of the metals recovered [7,8]. The development of more efficient and greener recovery methods for these metals is therefore necessary in order to reduce the environmental impact by eliminating the need for harsh chemical processes and by preserving the original catalytic support so they can be reused in future applications.

Supercritical carbon dioxide ($scCO_2$) is an environmentally friendly, inexpensive, and readily available solvent, which is gaining attraction as an important commercial solvent in chemical extraction processes due to its low environmental impact [9]. Numerous publications in the literature are dedicated to the use of chelating agents in supercritical fluids for the extraction of metals [10–13]. The easily accessible critical parameters of CO_2 (T_c = 31 °C and P_c = 7.34 MPa) allow extractions to be performed at relatively low temperatures and pressures with minimal damage to the target compounds. Selective extractions can also be carried out by tuning the solvent properties due to the pressure-dependence of the solvent power of dense CO_2 for the desired compounds. Heavy metal extraction in $scCO_2$ has been discussed by Lin et al. [14] and Zhang et al. [15]. They have shown the successful extraction of Ni and Cu metal ions in supercritical CO_2 using oligo(vinyl acetate) bearing bipyridine moieties as a ligand. Iwao et al. [16] have reported the modification of $scCO_2$ with chelating agents for the extraction of palladium from solid catalysts in $scCO_2$.

Herein, we propose the use of functionalized fluorinated homopolymers and copolymers to extract palladium from porous alumina supports in $scCO_2$. The solubility of the polymers in dense CO_2 and their complexing ability to the Pd species (Pd nanoparticles) are keys to the success of this extraction technique. Highly $scCO_2$-soluble functional complexing polymers have been previously synthesized by RAFT and RITP polymerizations [17–22]. Previous work has also shown that thiols can complex well with Pd^0 [23–25] and Pd^{II} [26]. The phosphine functional group has also been shown in literature to be capable of complexing well with Pd^{II} and Pd^0 [25,27,28]. In the literature, Ramirez et al. [29] have shown that phosphine-containing ligands provided very good stability to Pd^0 nanoparticles and other organo-phosphorous ligands have been used by Koh et al. [30] in the extraction of various metal ions in $scCO_2$. The preparation and use of fluorinated phosphine Pd^{II} complexes in $scCO_2$ have also been reported by Carroll and Holmes [31].

In this work, we report the use of fluorinated homopolymers and gradient copolymers functionalized with a thiol and/or phosphine moiety for the extraction of palladium from a porous alumina support in $scCO_2$. Specifically, the thiol-terminated poly(1,1,2,2-tetrahydroperfluorodecyl acrylate) homopolymer PFDA-SH, a poly(1,1,2,2-tetrahydroperfluorodecyl acrylate-*co*-diphenylphosphinostyrene) gradient copolymer P(FDA-*co*-DPPS), and a thiol-terminated gradient copolymer P(FDA-*co*-DPPS)-SH have been selected for the extractions (Fig. 1). The FDA units provide excellent solubility of the polymers in $scCO_2$ while the thiol and phosphine functional groups act as complexing groups. Commercial Pd/Al_2O_3 catalysts (beads and pellets with 0.5 wt.% and 5 wt.% Pd loading, respectively) were used for the assessment of polymer-assisted extraction of palladium in $scCO_2$ from the Pd/Al_2O_3 catalysts.

2. Materials and methods

2.1. Materials

Two types of catalytic supports were used in this work. Palladium on 3 mm alumina beads at a loading of 0.5 wt.% (Pd/Al_2O_3, Aldrich, 0.5%) and palladium on 3 mm alumina pellets at a loading of 5 wt.% (Pd/Al_2O_3, Alfa Aesar, 5%) were used as received. 1,1,2,2-tetrahydroperfluorodecyl acrylate (FDA, Elf Atochem) was vacuum distilled, passed through activated basic alumina, and filtered through a 0.2 µm PTFE filter before use. α, α, α − trifluorotoluene (TFT, Aldrich, > 99%) was distilled before use. 2,2′-Azobis(2-methylpropionitrile) (AIBN, Fluka, 98%) was purified by recrystallization in methanol and dried under vacuum before use. The chain transfer agent ethyl-2-(phenylcarbonothioylthio)propionate (chain transfer agent, CTA) was synthesized and purified before use as described in a previous paper [32]. Deionized water (DIW) (1 µS cm^{-1}) was obtained using a D8 ion exchange demineraliser from A2E Affinage de L'Eau. Butylamine (Aldrich, 99.5%), triphenylphosphine (PPh_3, Aldrich, 99%), 4-(diphenylphosphino)styrene (DPPS, Aldrich, 97%), activated basic Brockmann I aluminum oxide (Aldrich), S-(thiobenzoyl)thioglycolic acid (Aldrich, 99%), sodium hydroxide (NaOH, Fisher), hydrochloric acid (HCl, Aldrich, 37%), sodium sulfate (Aldrich, > 99%), ethyl 2-mercaptopropionate (Alfa Aesar, 98%), methanol (Aldrich, 99%), 1,1,2-trichlorotrifluoroethane (CFC113, Freon 113, Aldrich, 99%), and carbon dioxide (CO_2, SFE 5.2, Linde Gas SA, France, 99.9%) were used as received.

2.2. Polymer synthesis by RAFT

The polymers PFDA-SH, P(FDA-*co*-DPPS) and P(FDA-*co*-DPPS)-SH were synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization according to the following procedure. For the synthesis of PFDA homopolymer, the monomer FDA, solvent TFT, radical initiator AIBN, and the chain transfer agent (CTA) ethyl-2-(phenylcarbonothioylthio)propionate were mixed in a round-bottom Schlenk flask equipped with a stir bar and sealed with a septum and parafilm. The molar concentration of AIBN to CTA was kept constant at 0.3 and the concentration of monomer to TFT was kept at 1.1 g mL^{-1}. The targeted theoretical molecular weight ($M_{n,targeted}$ = (mass of monomer)/(moles of CTA) + M_{CTA}) was 18,500 g mol^{-1}. Following a 30 min purge of the reaction mixture with argon, the reaction was started by immersing the flask into a 65 °C oil bath, under agitation with a magnetic stir bar. The flask was kept under an argon

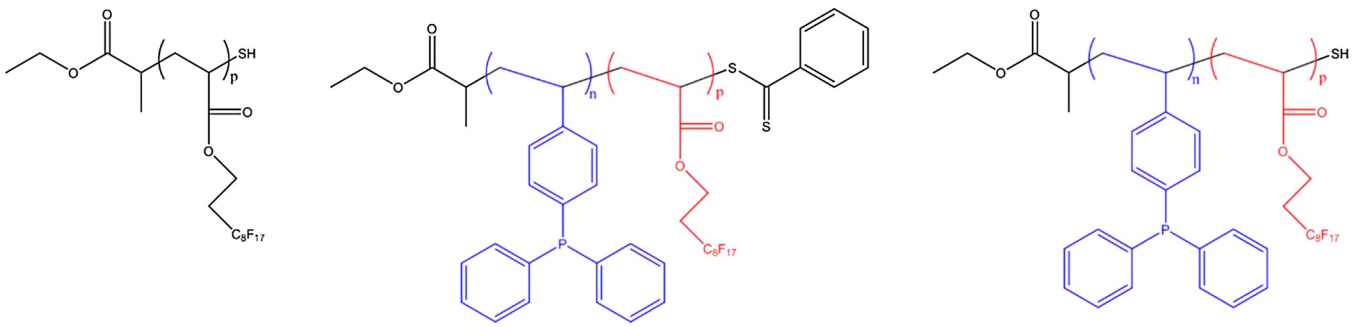

Fig. 1. Functional fluorinated polymers used in the extraction of Pd in supercritical CO_2: PFDA-SH (left), P(FDA-*co*-DPPS) (middle), and P(FDA-*co*-DPPS)-SH (right).

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