A step towards circular economy of critical minerals: polymer-assisted supercritical CO_2 extraction of Pd from spent supported catalysts

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1. Introduction

The list of critical minerals is continuously increasing over the years (rare earths, platinum group elements, niobium, tantalum, indium, tungsten, cobalt, lithium,...).[1-5] Among these minerals, platinum group metals are of high interest mainly due to their exceptional catalytic properties. In recent works, we have started to explore an environmentally-friendly process for the extraction of Pd from supported catalysts by polymer-assisted supercritical CO_2 extraction. Previously, we have reported some promising results starting from virgin supported catalysts.[6-8] In this presentation, we will present new unpublished results starting from a spent supported catalyst (Figure 1), as well as some data for the recovery of the Pd from the extracted Pd/polymer mixture.

2. Materials and Methods

Gradient copolymers of 1,1,2,2-tetrahydroperfluorodecyl acrylate (FDA) and diphenylphophinostyrene (DPPS) or 4-vinylpyridine (4-VP) were synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization and their solubility in supercritical CO_2 was assessed by cloud point determination. An industrial spent catalyst composed of 0.5 wt% Pd supported on alumina (Al_2O_3), was fully characterized (ICP-OES, XPS, TEM, BET) and pre-treated by reduction (H_2) and oxidation (Cl_2) steps to favor the subsequent extraction of Pd. Extraction experiments were performed using supercritical CO_2 in the presence of the complexing polymers P(DPPS-*grad*-FDA) or P(4-VP-*grad*-FDA), in either a 35 mL stainless-steel extraction cell followed by a simple bubbling collector flask or a 250 mL stainless-steel extractor followed by a pressure-controlled stainless-steel separator with sapphire windows.

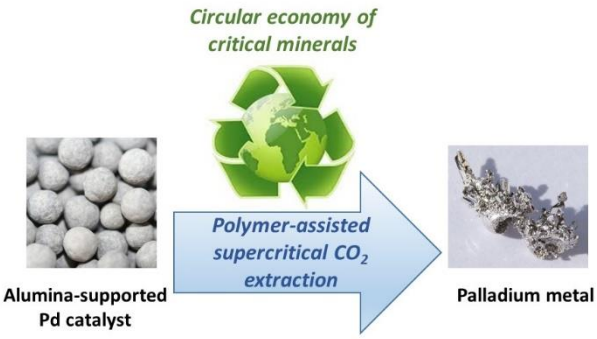

Figure 1. Recycling of Pd from spent catalyst by polymer-assisted supercritical CO_2 extraction.

3. Results and discussion

Gradient copolymers P(DPPS-*grad*-FDA) or P(4-VP-*grad*-FDA) prepared by RAFT polymerization have been shown to be soluble in dense CO_2 (liquid and supercritical CO_2) at low CO_2 pressure. For instance, P($DPPS_5$-*grad*-FDA_{13}) showed cloud point pressures as low as 88 bar at T= 25.4°C, and 138 bar at T= 39°C, for a polymer concentration of 1 wt% versus CO_2.

The pristine industrial spent catalyst was composed of 100% palladium oxide (PdO) nanoparticles of D_n= 2 nm in diameter, supported on large alumina beads of ~5 mm in diameter, with 1 wt% total carbon. After thermal treatment with H_2 then Cl_2, the treated spent catalyst was composed of 11% PdO and 89% of chlorinated Pd species ($PdCl_2$ and/or Na_2PdCl_4) (determined by XPS), with no detectable residual carbon.

The polymer-assisted extraction of Pd from the pristine spent catalyst in supercritical CO_2 at T=40°C and 250 bar was negligible (5% extraction conversion). In contrast, the P(DPPS-*grad*-FDA)-assisted extraction allowed for removal of 61% of Pd from the pre-treated catalytic support, and 100% of the extracted Pd was recovered as a polymer/metal mixture. The separation of the metal from the polymer was possible by a back extraction post-treatment using an aqueous solution of HCl and H_2O_2 (96% efficiency). The P(4-VP-*grad*-FDA) was also similarly able to extract Pd from the pre-treated alumina catalytic support. A preliminary economical assessment based on lab scale data showed that the OPEX and CAPEX of this environmentally-friendly supercritical CO_2 extraction process itself (outside the pre- and post-treatments) are in the range of a conventional leaching process.

4. Conclusions

It has been demonstrated that CO_2-soluble complexing copolymers, such as P(DPPS-*grad*-FDA) and P(4-VP-*grad*-FDA), are able to remove Pd (61% removal without optimization) from a spent alumina-supported catalyst by supercritical CO_2 extraction at moderate temperature (T = 40°C) and pressure (P = 250 bar), with complete recovery of the extracted critical metal. These results open the route for new opportunities in the development of sustainable processes based on supercritical fluids science and technology regarding the circular economy of other critical metals, such as platinum (fuel cells) and cobalt (Li-ion batteries). Indeed, these critical minerals are key raw materials to face the environmental challenges and to favor clean energy transitions.

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