

Extraction of rhodium from supported liquid-phase hydroformylation catalysts with supercritical carbon dioxide

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ABSTRACT

The continuous extraction of the rhodium inventory in supported liquid-phase (SLP) catalytic materials utilized in the hydroformylation (HyFo) of 1-butene was investigated by supercritical carbon dioxide (scCO₂). Optimization of extraction efficiency involved varying parameters such as temperature (90 and 120 °C), pressure (10, 20 and 30 MPa), and the addition of methanol as a polar co-feed to the extraction medium (0–20 vol%). The results underscored the critical role of methanol in facilitating extraction, as experiments employing pure scCO₂ yielded no rhodium recovery. Furthermore, extraction performance demonstrated sensitivity to temperature and pressure adjustments during the process. Notably, the use of 10 vol% methanol at 120 °C and 30 MPa achieved complete rhodium extraction from the grained SLP materials, which was identified as the optimum extraction condition. This study highlights the potential for scaling up in-situ rhodium extraction processes within HyFo production plants based on SLP catalysts, emphasizing significant implications for industrial applications.

1. Introduction

Hydroformylation (HyFo) is one of the largest homogeneously catalyzed reactions in industry with an annual production of more than 12 million tons of aldehydes [1–5]. The aldehydes are formed by the reaction of olefins with syngas (CO/H₂) and the products are applied as important intermediates in the manufacturing of valuable chemical building blocks, such as alcohols, amines, carboxylic acids or nitriles [6].

Rhodium (Rh) complex-based supported liquid-phase (SLP) catalyst systems show great potential in continuous flow gas-phase HyFo, thus presenting an alternative to conventional continuous stirred-tank reactor systems [7–11]. In these systems the catalytic components are immobilized on a porous, solid support such as a cylindrical monolithic SiC material characterized by an exceptional mechanical resistance and prominent thermal conductivity [12]. The monoliths may be washed with SiO₂ nanoparticles, effectively creating mesoporosity, which plays a crucial role in preventing leaching of the liquid catalyst phase [13,14]. Additionally, a polymeric membrane can be applied to the external surface of the monoliths, enabling selective in-situ separation of the formed aldehyde products and thereby suppressing the

formation of aldol condensation byproducts [15,16].

Rh-SLP catalysts based on SiC monolithic supports are currently under development for industrial, large-scale butene HyFo [17–19]. Besides the Rh metal, the system comprises a diphosphite ligand (biphephos) that ensures excellent regioselectivity towards the desired linear aldehyde product (n-pentanal) and catalyzes the tandem isomerization reaction in cost-effective raffinate feedstock, which is rich in 2-butene [3,20,21]. Additionally, the system also comprises the additive sebacate, which serves as an involatile liquid phase at operating temperatures (>90 °C). Due to the low solubility of n-pentanal in sebacate, the accumulation of undesired high-boiling byproducts (aldols) in the liquid phase is significantly suppressed leading to enhanced catalytic activity [15,22]. The SLP concept with monolithic SiC support as well as chemical structures of the catalyst components in the liquid phase are depicted in Fig. 1.

Rh is a highly expensive metal produced on a global scale of only around 30 tons per year as a by-product of copper and nickel refining [23]. Despite its scarcity, Rh is an important component in many applications such as jewelry, electrical/electronic devices, and dental materials besides catalysts for HyFo (and other homogeneous processes)

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[24], automotive exhaust cleaning [25], and hydrotreating of fossil/biomass resources to fuels [26–29]. Several techniques have been reported in the literature for recovering Rh from solid chemical wastes, including hydro-, iono- and pyrometallurgical as well as biological treatments [30–41]. However, wet/thermal treatments pose challenges for large-scale industrial applications due to their high costs, secondary waste generation, and energy consumption. Biological processes also face limitations due to the sensitivity of microorganisms to external environmental factors [42].

Supercritical CO₂ (scCO₂) extraction represents a significant advancement in sustainability compared to conventional recovery techniques owing to the utilization of scCO₂'s unique properties: abundant availability, tunable solvent power, and the ability to operate under relatively mild conditions to achieve the supercritical state ($T_c = 31.1\text{ }^\circ\text{C}$, $P_c = 7.38\text{ MPa}$) [43–45]. The scCO₂ technology is also advantageous as a CO₂ utilization strategy, where CO₂ can be converted into valuable chemicals such as polymers [46], aviation fuels [47,48], and C1 products [49–52], or utilized in processes that facilitate the extraction and recovery of precious metals [53–55]. Although scCO₂ processes may require substantial capital investment for specialized high-pressure equipment, its adjustable properties such as density and viscosity, can enhance extraction efficiency and potentially mitigate some operational costs. ScCO₂ exhibits density comparable to that of a liquid and a viscosity resembling that of a gas [42], and these attributes are particularly advantageous for extraction applications as they can be adjusted by temperature and pressure to optimize extraction efficiency [56–58]. The increased density of scCO₂ enhances its dissolution ability, improving the overall efficiency of the extraction process [59]. Meanwhile, its low viscosity enables it to easily penetrate porous, solid materials, thereby facilitating the diffusion of CO₂ and the extraction of desired compounds [56]. Despite these advantages, scCO₂'s inherently non-polar nature poses limitations in solubilizing more polar compounds. However, the solvent power of scCO₂ for more polar compounds can be significantly enhanced by inclusion of a polar co-feed, such as methanol [60–62].

To ensure long-term sustainable operation of the HyFo Rh-biphephos-sebacate SLP catalyst system, a robust approach for

recovering of the Rh inventory as well as an effective metal recycling strategy is demanded [63,64]. Solubility predictions of the components in the catalyst system by Conductor-like Screening Model for Real Solvents (COSMO-RS) have predicted a relatively higher solubility of sebacate in hexane (i.e., non-polar solvent) compared to biphephos [65]. However, both components demonstrated higher solubility in more polar solvents such as dichloromethane (DCM) and methyl *tert*-butyl ether (MTBE). Table S1 provides solubility predictions of sebacate and biphephos in these solvents.

In this study, systematic screening is performed of co-feed variations on the scCO₂ extraction of Rh from the Rh-biphephos-sebacate SLP catalyst system, along with an assessment of extraction conditions such as temperature and pressure. In perspective, such scCO₂ extraction process may provide potential for recovery of the Rh inventory from HyFo SLP systems in monolithic or fixed-bed reactors by in-situ stripping the support within the reactor by simple adjustment of the feed composition after a specific operational period.

2. Materials and methods

2.1. Preparation of SLP materials

2.1.1. Grained samples

A tubular monolithic SiC support (200 mm × 25.4 mm) containing 70 nm SiO₂ particles (LiqTech A/S) [14] were crushed and fractionated to obtain a 90–250 μm fraction size (Figure S1). The fraction was subsequently treated under vacuum ($\leq 1\text{ mbar}$) at room temperature overnight and then subjected to incipient wetness impregnation with a catalyst stock solution containing the Rh precursor dicarbonyl(acetylacetonato) rhodium(I) (Rh(acac)(CO)₂, >98 %, Sigma-Aldrich), the ligand (6,6'-[(3,3'-di-*tert*-butyl-5,5'-dimethoxy-1,1'-biphenyl-2,2'-diyl)bis(oxy)]-bis(dibenzo[*d,f*][1–3]-dioxaphosphepin) (biphephos, >98 %, Evonik Oxeno GmbH), and the additive bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate (sebacate, >98 %, Evonik Oxeno GmbH).

The catalyst components were dissolved in the molar ratios of 1/4/

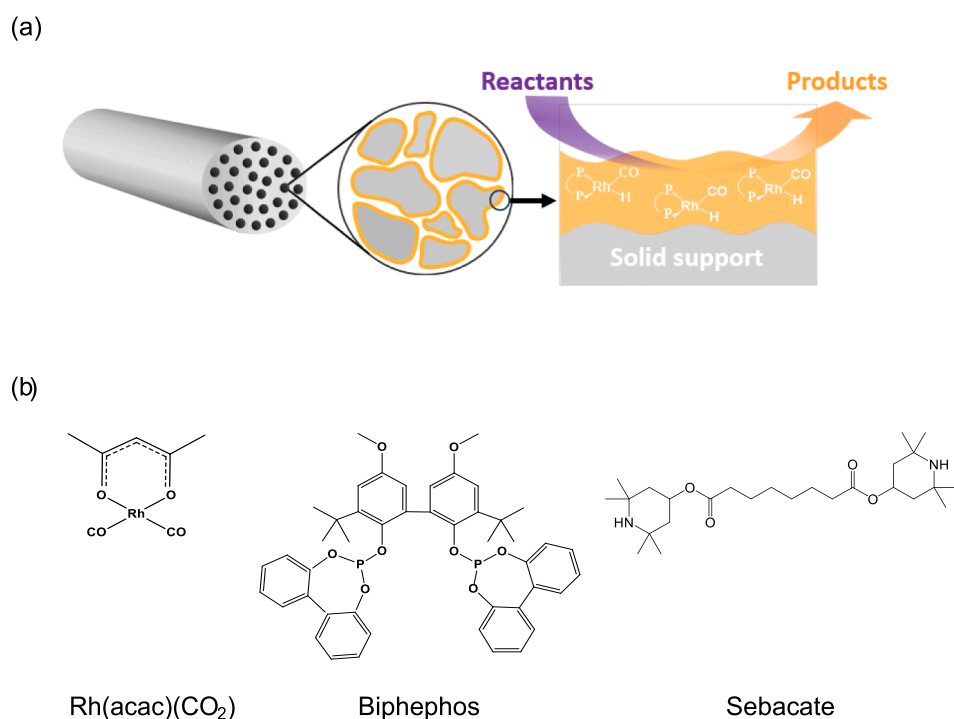


Fig. 1. (a) Schematic illustration of SLP material composed of monolithic SiC support infiltrated by SiO₂ nanoparticles; (b) chemical structures of the catalyst components within the liquid phase of the SLP material.

16 (Rh/biphephos/sebacate) in 40 mL anhydrous CH₂Cl₂ ($\geq 99.8\%$, Sigma-Aldrich) under a nitrogen atmosphere (99.999%, Air Liquide) using standard Schlenk technique, resulting in concentrations of Rh, biphephos and sebacate of 1.1, 13.4 and 32.7 g L⁻¹, respectively. After the impregnation, the sample was dried at room temperature under a nitrogen flow (200 mL min⁻¹) for 2 h followed by drying under vacuum (≤ 1 mbar). This process resulted in a final SLP material with loadings of 0.02 wt% Rh, 0.74 wt% biphephos, and 1.82 wt% sebacate.

2.1.2. Monolithic samples

The tubular monolithic SiC support was impregnated with molar ratios of Rh/biphephos/sebacate of 1/4/16 using an anhydrous CH₂Cl₂ ($\geq 99.8\%$, Sigma-Aldrich) stock solution (1.7 g L⁻¹ Rh, 21 g L⁻¹ biphephos and 51 g L⁻¹ sebacate) by a previously described procedure [13].

2.2. Extraction of SLP materials using scCO₂

Grained and monolithic SLP samples (both pre- and post-HyFo reaction) were extracted with scCO₂ using the flow apparatus depicted in Figure S2. CO₂ ($>99.995\%$, Messer Austria GmbH) was cooled to $-7\text{ }^{\circ}\text{C}$ by a recirculating cooler (CF 40, JULABO GmbH) and introduced into the system through two CO₂ pumps (PU-2086Plus, Jasco) with cooled heads. A high-performance liquid chromatography (HPLC) pump (PU-2089Plus, Jasco) was used to deliver methanol co-feed.

In the extraction of grained SLP samples, 2.0 g of fractionized sample was loaded into a stainless-steel HPLC column (250 mm \times 4.6 mm \times 1/4" OD, 2 μm frits, 4.15 mL volume; Restek) and heated up to 120 $^{\circ}\text{C}$ in an HPLC column heater system (Brinkmann CH-500, Metrohm). For the extraction of monolithic samples, the monolith was placed into a 180 mL extractor with an internal diameter of 29.6 mm and a length of 250 mm, then heated to 80 $^{\circ}\text{C}$ in an oven (CO-2060Plus, Jasco). A back pressure regulator (BP-2080Plus, Jasco; temperature set to 60 $^{\circ}\text{C}$) was used to set the desired pressure for the extractions of both the grained and monolithic samples, respectively. Upon passing through a gas-liquid separator, the extracts were collected in the collection vessels. The total feed flow rate was maintained constant at 4 mL min⁻¹ throughout all experiments, with an extraction time of 2 h consistently applied. The extraction temperatures and pressures were varied for the SLP samples between 10 and 30 MPa and 80–120 $^{\circ}\text{C}$.

The extraction efficiency of compound *x* (Rh or sebacate) was determined according to Eq. (1):

$$\text{Extraction efficiency (\%)} = [1 - (C_{e,x} / C_{i,x})] \times 100 \quad (1)$$

where $C_{i,x}$ represents the initial concentration of the compound *x* in the SLP material before extraction, and $C_{e,x}$ represents the concentration of *x* in the extract after scCO₂ extraction.

2.3. Analysis of components from SLP materials

2.3.1. Nuclear magnetic resonance (NMR) spectroscopy

The amounts of recovered sebacate from the scCO₂ treated SLP samples were analyzed by ¹H NMR spectroscopy on a Bruker Advance UltraShield 400 MHz spectrometer using TMS (tetramethylsilane) as internal standard. To prepare the samples for NMR analysis, the methanol co-feed from all extracts was evaporated under vacuum (40 $^{\circ}\text{C}$, 300 mbar), and the resulting material dissolved in CDCl₃ (99.8%, Eurisotop). To 0.5 mL aliquot of the CDCl₃ solution was added 1–2 mg naphthalene (99%, Merck) as external standard for the quantification.

2.3.2. Microwave digestion of scCO₂ extracts

After the NMR analysis, 0.5 g of aluminum oxide (activated, neutral, Brockmann Grade I, 58 Å, ThermoScientific) was added to the extracts to improve the handling of the small quantity of the recovered material. The CDCl₃ solvent was then evaporated under vacuum (40 $^{\circ}\text{C}$, 470

mbar) from the mixture and the resulting material dried in a vacuum oven at 50 $^{\circ}\text{C}$ overnight. After homogenizing with a mortar, 20–100 mg of the material was digested in 10 mL conc. aqua regia (freshly prepared from conc. HNO₃ and conc. HCl in a volume ratio of 1:3) in a microwave oven (Multiwave 5000, Anton Paar) using a temperature program consisting of 10 min linear heating from room temperature to 200 $^{\circ}\text{C}$ and a holding time of 20 min at 200 $^{\circ}\text{C}$ before cooling to room temperature at maximum rate. Subsequently, the digests were transferred to 15 mL centrifuge vials and filled with MilliQ water to a total volume of 15 mL.

2.3.3. Microwave digestion of SLP materials

Besides the digestion of extracts after scCO₂ extraction, some of the SLP materials (including the SiO₂/SiC support) were digested in a solution containing 1 mL of 40% aq. HF (p.a., Suprapur®) and 9 mL conc. aqua regia using the same microwave digestion procedure as described for the scCO₂ extracts in Section 2.3.2. The corresponding SLP materials included both freshly prepared SLP (without any extraction process) and SLP material that had already undergone scCO₂ treatment.

2.3.4. Analysis of the recovered Rh

The microwave digested samples were quantitatively analyzed for Rh by inductively coupled plasma mass spectrometry (ICP-MS, iCap Q, ThermoFisher Scientific). A calibration curve (Figure S3) was established using a series of five standards spanning the range of 0.1–25 ng g⁻¹ for Rh. The standards were derived from dilution of a certified single element standard solution of 1000 $\mu\text{g g}^{-1}$ Rh (Merck Millipore). Both the standards and sample solutions were diluted with 5% aq. HCl before analysis and each dilution step was performed gravimetrically. Each digested sample was diluted by a factor of 100–400. The dilution factor was individually calculated based on the available mass of scCO₂ extract to result in a predicted concentration of approximately 10 ng g⁻¹ in the measurement solution when assuming quantitative recovery of Rh in the extraction. Finally, each standard and measurement solution were spiked with Indium (In), serving as internal standard at a concentration level of 1 ng g⁻¹. Three replicates for each sample were measured. The measurement parameters are shown in Table S2.

Figure S4 represents the workflow of the extracts' treatment methods.

3. Results and discussion

3.1. Extraction from grained SLP samples

The Rh extraction efficiency with scCO₂ was examined for grained SLP samples by variation of several parameters, including pressure, temperature, and methanol co-feed content. Fig. 2 illustrates the effect of pressure on the extraction efficiency at constant temperature of 120 $^{\circ}\text{C}$ and methanol co-feed content of 10 vol% of the total flow. As shown in Fig. 2, quantitative Rh recovery was obtained from the grained SLP materials with a pressure of 30 MPa, whereas lower pressures of 10 and 20 MPa yielded lower efficiencies corresponding to about 75% Rh recovery. Increasing the pressure likely enhanced the solvent power of the supercritical fluid due to its higher corresponding density, leading to an increase in the solubility of the Rh complexes in the scCO₂ phase [59, 66].

In addition to Rh analysis, the quantities of extracted sebacate were also assessed at different pressures for the grained samples using ¹H NMR. The corresponding protons of each compound in the scCO₂ extracts are illustrated in Figure S5, and the ¹H NMR spectra of the extracted compounds are shown in Figure S6. The detailed quantification procedure is described in equations S1 and S2 in the supporting information. The recovered amounts of sebacate also increased with pressure, further supporting the increased solvent power of scCO₂ with higher pressure. Unfortunately, the biphephos ligand degraded partly by the extraction procedure making quantification unfeasible (Figure S7).

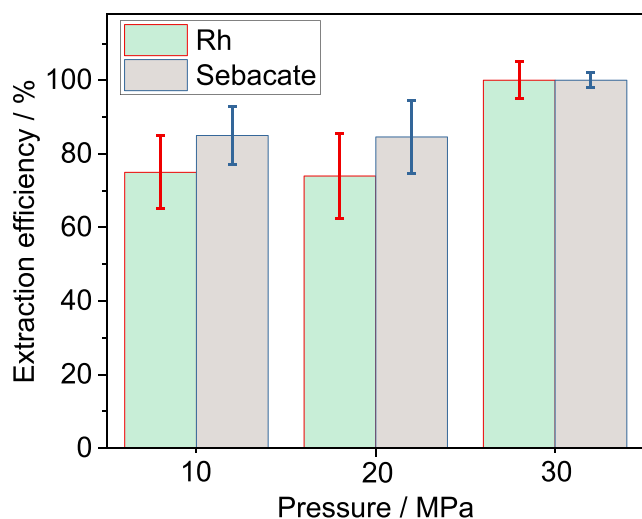


Fig. 2. Effect of pressure on the extraction efficiency of Rh and sebacate on grained SLP samples at 120 °C with a 10 vol% methanol co-feed (total flow: 4 mL min⁻¹).

Besides variations in pressure, a lower extraction temperature of 90 °C was also examined for the grained SLP material at the optimized pressure of 30 MPa and a methanol co-feed content of 10 vol% (Fig. 3). Here, 79 % of Rh and 71 % of sebacate were recovered which were slightly less than achieved at the increased temperature of 120 °C. Elevating the temperature at a constant pressure can potentially increase the vapor pressure of the solutes, leading to enhanced dissolution of the components in scCO₂ and improving the extraction efficiency [59]. The sebacate recovery analysis by ¹H NMR also showed a similar trend of increased scCO₂ extraction efficiency at higher temperatures.

The preferred scCO₂ extraction temperature and pressure of 120 °C and 30 MPa, respectively, were selected for studying the effect of methanol co-feed variations in the total feed. Fig. 4 illustrates the amount of recovered Rh for methanol co-feed variations between 0 and 20 vol%. The results indicate an almost linear dependency between the amount of Rh recovered and the methanol concentration in the constant total flow of scCO₂ and methanol at lower methanol flows (0–5 vol%). Hence, with the pure scCO₂ medium (no methanol) the share of recovered Rh was very low around only 3 %, emphasizing the importance of

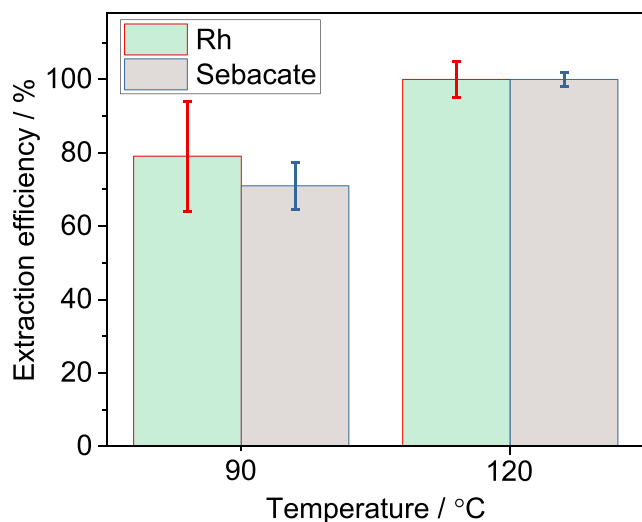


Fig. 3. Effect of temperature on the extraction efficiency of Rh and sebacate on grained SLP samples at 30 MPa with a 10 vol% methanol co-feed (total flow: 4 mL min⁻¹).

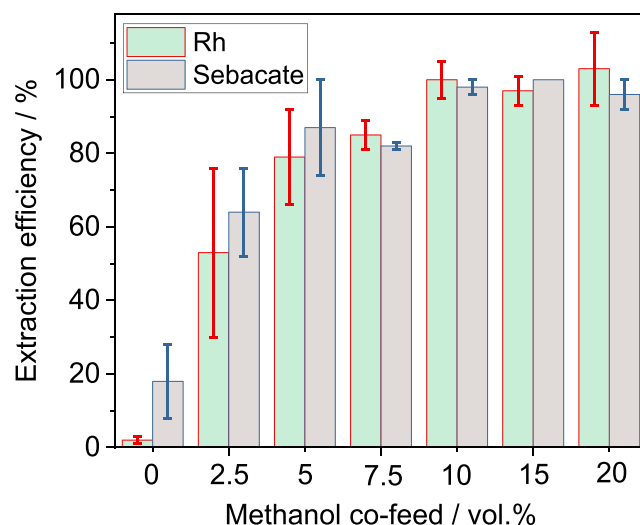


Fig. 4. Effect of methanol co-feed from 0 to 20 vol% on the extraction efficiency of Rh and sebacate at 120 °C and 30 MPa pressure (total flow: 4 mL min⁻¹).

adding methanol to the feed. With increased methanol concentration, the Rh recovery further increased reaching essentially full recovery with 10 vol% methanol in the feed, thus showing this co-feed concentration to be favorable at the given conditions.

Based on the results of varying the methanol content, it is evident that scCO₂ alone exhibits low solvent power for dissolving the Rh-biphenos-sebacate catalyst system. However, increasing the polarity of the feed enhances the extraction performance. This observation suggests that the ligand and Rh complexes cannot be fully dissolved in pure non-polar scCO₂ due to their slightly polar nature. This finding is consistent with a previous study, which showed an increased solubility of pyridine-2,6-dicarboxylic acid in a ternary system with scCO₂ and methanol (0.17–18.1·10⁻⁵ mol mol_{total}⁻¹) compared to a binary system with pure scCO₂ (0.44–3.4·10⁻⁶ mol mol_{total}⁻¹) at pressures of 10–20 MPa and temperatures of 40–60 °C [67].

The quantitative ¹H NMR analysis used to determine the amounts of extracted sebacate (Fig. 4), also shows a linear increase in recoveries with low methanol co-feed. The recovery continued to increase also at higher methanol concentrations but with smaller increments, particularly beyond 10 vol% where the extraction efficiency was almost quantitative. These results highlight the crucial role of methanol in enhancing solubility and overall extraction efficiency.

To validate the analytical methods used for obtaining the Rh recovery results, fresh grained samples (prior to scCO₂ extraction) were subjected to acid digestion using an HF-aqua regia mixture at 200 °C in a microwave digestion system. This process ensured that the entire SLP material, including the SiO₂/SiC support, was fully digested. The Rh content recovered from these samples was quantified at 105 % (±5 % standard deviation), thereby confirming the initial Rh content in the fresh SLP material and validating the accuracy of the analytical procedures employed (Figure S8).

Furthermore, grained samples extracted with methanol co-feed (7.5 and 10 vol%) underwent the same HF-aqua regia digestion process to allow determining the residual Rh content remaining in the support and thus not extracted by the scCO₂ medium. The residual Rh content was here not extracted but at 3–5 % (Figure S8), confirming that using the scCO₂ extraction method the Rh was indeed essentially completely extracted by scCO₂.

3.2. Extraction from monolithic SLP samples

Two monolithic SLP samples, including a freshly impregnated

monolith with the Rh-biphephos-sebacate catalyst system (pre-HyFo monolith) and the same monolith used in the HyFo reaction (post-HyFo monolith), were subjected to scCO₂ extraction using 5 vol% methanol co-feed at 80 °C and 15 MPa of pressure. The extraction method for monolithic samples was performed under milder conditions than the grained samples due to instrument limitations regarding the use of much larger samples (i.e., monolith had the size 200 mm × 25.4 mm).

For both monolithic samples, only 1–2 % of the Rh was extracted suggesting that the scCO₂ technique under these conditions is not effective for monolithic samples. This ineffectiveness could potentially be due to the larger extractor size and the reduced surface area of the monolithic samples, resulting in lower solvent power on a mass basis and less exposure of the extraction medium to the sample. Additionally, milder extraction conditions are expected to further reduce the extraction efficiency for the monolithic materials, as also shown in Section 3.1 for the grained SLP samples where higher pressure and temperature enhanced the extraction efficiency. The CO₂ flow patterns within the extractor might also pose limitations to the extraction efficiency, as uneven flow distribution could hinder the effective contact between the CO₂ and the sample. Accordingly, enhancing and optimizing the extraction process for monolithic SLP samples will be the focus of future work.

4. Conclusions

The precious Rh metal inventory contained in Rh-biphephos-sebacate SLP catalyst systems targeted for industrial 1-butene HyFo was successfully and completely extracted with scCO₂ as extraction medium. This highly effective scCO₂ extraction method does not require any specific pretreatment of the samples, such as adding different complexing agents or employing harsh extraction conditions. The scCO₂ extraction conditions were optimized by screening different parameters such as temperature, pressure, and methanol co-feed. Among these conditions, a temperature of 120 °C and a pressure of 30 MPa were determined to be preferred, as higher pressure and temperature increased the solvent power of the supercritical fluid, resulting in enhanced extraction efficiency. The addition of the methanol co-feed was found necessary because its higher polarity is beneficial for the extraction. The optimized methanol co-feed content was found to be 10 vol% of the total flow (4 mL min⁻¹). Overall, the study provides proof of concept for extracting Rh metal from crushed monolithic SLP materials under various scCO₂ conditions, and scaling up and implementing the in-situ recycling process on monolithic catalysts will be the focus of future investigations.

CRediT authorship contribution statement

Mahtab Madani: Writing – original draft, Visualization, Methodology, Investigation. **Leonhard Schill:** Writing – review & editing, Supervision, Methodology. **Blete Hulaj:** Writing – review & editing, Validation. **Jakob Willner:** Writing – review & editing, Formal analysis. **Andreas Limbeck:** Writing – review & editing, Resources. **Katharina Bica-Schröder:** Writing – review & editing, Resources, Methodology. **Rasmus Fehrmann:** Writing – review & editing, Supervision. **Anders Riisager:** Writing – review & editing, Supervision, Resources, Methodology, Funding acquisition, Conceptualization.

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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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jcou.2024.102968](https://doi.org/10.1016/j.jcou.2024.102968).

Data Availability

Data will be made available on request.

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