SYNTHESIS, CHARACTERIZATION, AND APPLICATION OF SUPPORTED POLYMERIC IONIC LIQUIDS (polySILPs)

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The supported ionic liquid phase (SILP) technology is a fundamental and novel approach to obtain a thin layer of ionic liquid dispersed onto the surface of a porous solid with high surface area (*e.g.* silica). Ionic liquids (ILs) constitute a special class of materials, which are generally liquid at temperatures below 100 °C, composed solely of ions. They often possess unique physicochemical properties, such as negligible vapor pressure, wide solubility range, and broad electrochemical conductivity, to name a few. These properties can be attributed to the synergistic and cooperative effects between their composing ions. Hence, by appropriate selection of the ions, it is possible to transfer specific properties of the liquid to the solid surface by immobilizing the fluid on the surface [1]. Thus, the SILP concept allows to access "designer surfaces" with unique surface properties, which are otherwise impossible to obtain with the available synthetic approaches.

Characterization data

PolySILP materials with different loadings [10-50% (w/w)] were prepared. Apart from the gravimetric data, a number of characterization techniques, such as DRIFT-IR, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC) were conducted for the systematic characterization of these materials. Prior to each analysis, the samples were dried overnight to a residual pressure of 0.1 mbar in order to eliminate interferences due to the absorbed water molecules. The thermal decomposition temperatures of these materials were found to be higher than 350 °C. In the IR spectra, peaks in the region of 2500-3500 cm⁻¹ and in the region of 1400-2000 cm⁻¹ suggests the successful loading of the polymer on the silica surface.

TGA curves of 3

DRIFT-IR spectra of 3



Synthesis of supported ionic liquids



Application for metal separation

The growing demand for Platinum Group Metals (PGMs) for a variety of applications is foreseen to create a supply deficit in the coming years. Their limited and geographically restricted natural resources have rendered their effective recycling imperative as a means of minimizing the supply-demand gap. The automotive industry is currently dominating the overall PGM demand, thus end of life car catalysts account for a significant amount of PGMs that can be recovered from secondary raw materials. The PLATIRUS project is dedicated to the development of novel PGM recycling approaches that will contribute to the sustainability goals of Europe as well as its independency from the international PGM market [5].



Source: Monolithos

The separation of PGMs is primarily based on solvent extraction methods, which albeit quite effective, are associated with a number of drawbacks. Namely, these include use of high solvent amounts thus waste, slow kinetics, emulsion formation, high environmental impact, and insufficient recovery rates. Supported ionic liquid phases (SILPs and polySILPs) are an attractive alternative approach to exploiting the advantages that ionic liquids have to offer while at the same time circumventing the problems accompanying liquid-based separations [6].

Immobilization of an ionic liquid onto a solid support is often achieved *via* either physisorption or covalent anchoring of a monolayer onto the support. In this study, silica 60 is employed as the mesoporous solid support. Suspension of silica 60 along with the solution of the IL $[P_{66614}]CI$ in dichloromethane at room temperature and subsequent evaporation of the solvent resulted in the physisorption of a thin IL layer on the silica surface. SILP materials with a range of IL loadings [10-50% (w/w)] were prepared.



A significant limitation of the SILP materials is the potential leaching of the IL phase from the support [2], which severely limits their usage. This phenomenon can be attributed to certain solubility of the IL in the mobile phase or to physical erosion, which occurs during extended exposure to the mobile phase. Employment of a layer of cross-linked polymeric ionic liquid onto the solid support (polySILP) represents an alternative approach to circumventing this issue. Since most of the physicochemical properties of the IL remain intact even after polymerization, these materials (polySILPs) can be utilized in a similar fashion like SILPs. Herein, the synthetic procedure of two different silica supported polymeric ionic liquid materials is presented. The polymerization was performed on a pre-functionalized silica surface *via* the thiol-ene reaction [3, 4].





The spent automotive catalyst was stirred in an acidic solution at certain conditions of time and temperature. The PGMs of the catalyst were leached into the acidic medium and the recovered leachate was diluted with water and forced through the polySILP with the application of constant air flow. The polySILP was packed in an "in-house" constructed column, comprising a glass pipette and polySILP **3**.

Different polySILP loadings of **3** [10, 20, 50% (w/w)] were tested for their retention behavior towards PGMs and other accompanying elements leached from the automotive catalyst matrix.

Retention of PGMs from model system



Retention of PGMs from autocatalyst leachate



Model solution in 8 M HCI: Pt 194 ppm, Pd 318 ppm, Rh 34 ppm Retention conditions: 2.5 g model solution, 0.5 g polySILP 20% Flow rate: 1.5 mL/min Real leachate in 8 M HCI: Pt 194 ppm, Pd 318 ppm, Rh 34 ppm Fe 777 ppm, Al 1012 ppm, Ce 1572 ppm Retention conditions: 2.5 g model solution, 0.5 g polySILP 20% Flow rate: 2.0 mL/min

The polySILP **3** with a 20% (w/w) loading combined with a leachate diluted with H_2O in a 1:7 ratio, demonstrated the capacity for almost complete separation of PGMs from the major interfering elements (AI, Fe, Ce) in a single separation step.

Conclusions

Novel silica supported polymeric ionic liquids (polySILPs) have been successfully synthesized and characterized. The presence of cross linkage in the polymeric IL layer and the covalent bonding with the solid support significantly reduce the possibility of IL leaching out of the solid material. More interestingly, polySILP **3** with 20% (w/w) loading has been employed for separation of platinum group metals (PGMs) and has demonstrated excellent efficiency for the selective separation of PGMs from other major interfering elements present in car catalysts in a single separation step.

References

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Acknowledgements

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No. 730224. Financial support from the Austrian Research Promotion Agency (FFG, project No. 859784) is also gratefully acknowledged.

