

Toward the recovery of platinum group metals from a spent automotive catalyst with supported ionic liquid phases

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Supporting information contains 16 pages

Supporting information contains 25 figures

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1. Synthesis of SILP P₆₆₆₁₄Cl 10% (w/w)

Silica 60 (Merck, size 40-60 μm , specific surface area 480-540 m^2/g) was pre-dried in vacuum oven at 50 $^\circ\text{C}$ for 24 h. A 250 ml round bottom flask was charged with 23.0 g silica-60 and 2.3 g P₆₆₆₁₄Cl. The mixture was suspended in 100 ml CH_2Cl_2 and shaken at room temperature until the complete amount of ionic liquid was dissolved. The solvent was removed carefully by reduced pressure. Remaining solvent traces were removed via high vacuum (10^{-2} mbar) for 24 h. The procedure was accordingly adapted for the preparation of 20% and 50% loadings.

2. Drift-IR spectra of SILPs

The spectra were recorded with a Bruker Vertex 80FTIR spectrophotometer using a narrow band MCT (mercury-cadmium-telluride) detector measuring diffuse reflectance. 256 scans were collected for each spectrum with 4 cm^{-1} resolution.

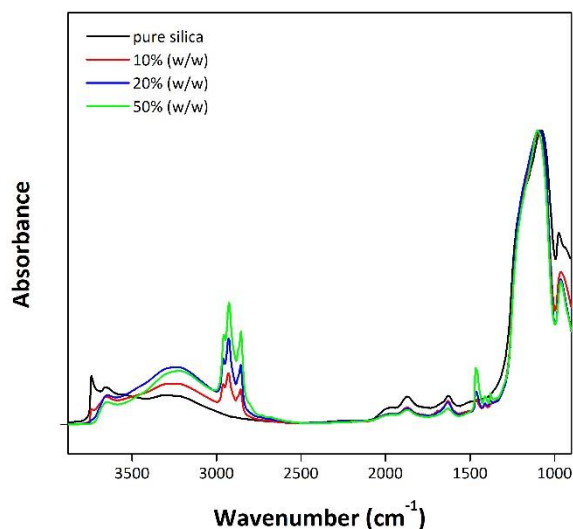


Figure S1 Drift-IR spectra of pure silica and SILPs with P₆₆₆₁₄Cl loadings of 10, 20 and 50% (w/w).

3. ATR-IR spectra of polySILPs

Recorded with a Bruker Vertex 80FTIR spectrophotometer using a DTGS (deuterated triglycine sulfate) detector measuring diffuse reflectance. For each spectrum, 512 scans were collected with 4 cm^{-1} resolution.

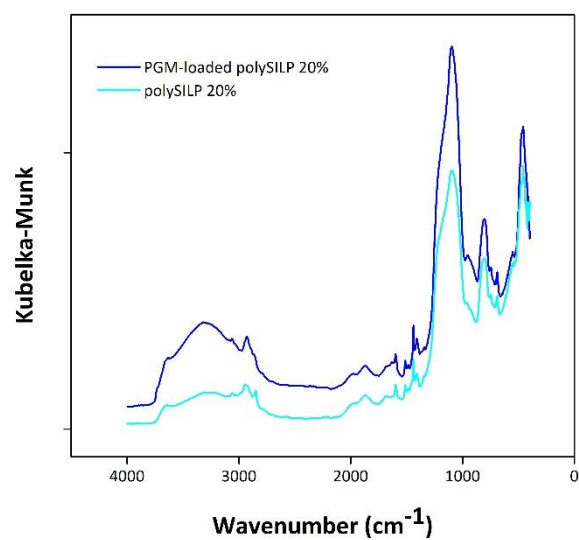


Figure S2 ATR-IR spectra of polySILP 20% and PGM-loaded polySILP 20%.

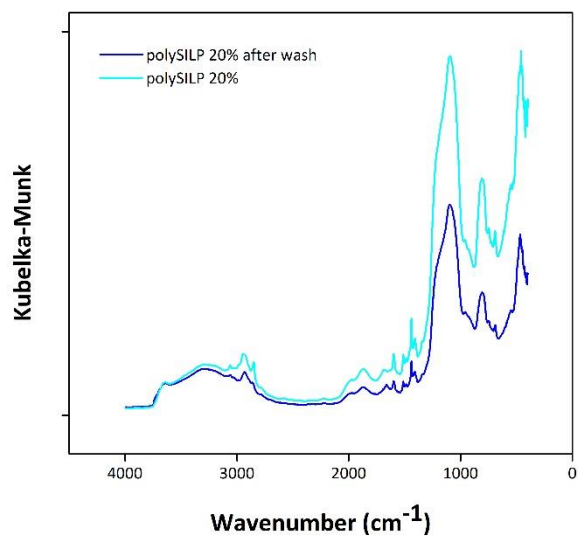


Figure S3 ATR-IR spectra of polySILP 20% and used polySILP 20% after washing with 0.1 M HCl.

4. SEM images of SILPs and polySILPs

The images were recorded with a FEI Quanta 200 microscope equipped with an EDAX Octane Pro detector. Data were processed with the Team Enhanced software.

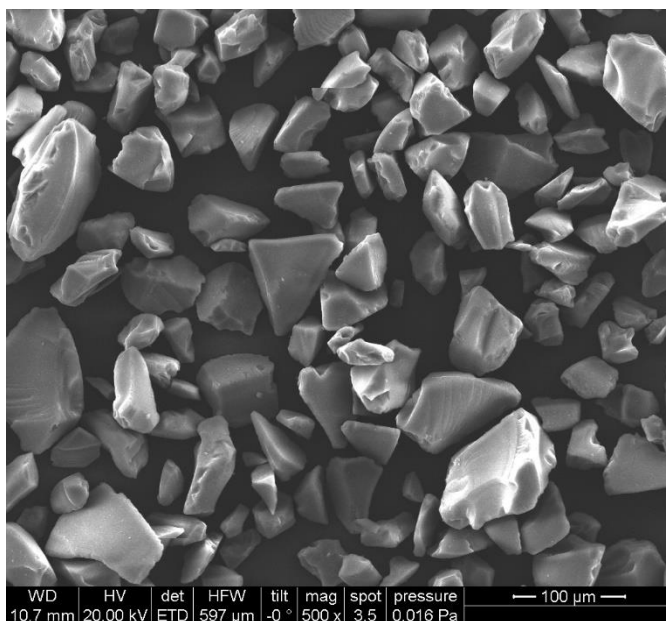


Figure S4 SEM image of SILP with P₆₆₆₁₄Cl loading of 20% (w/w).

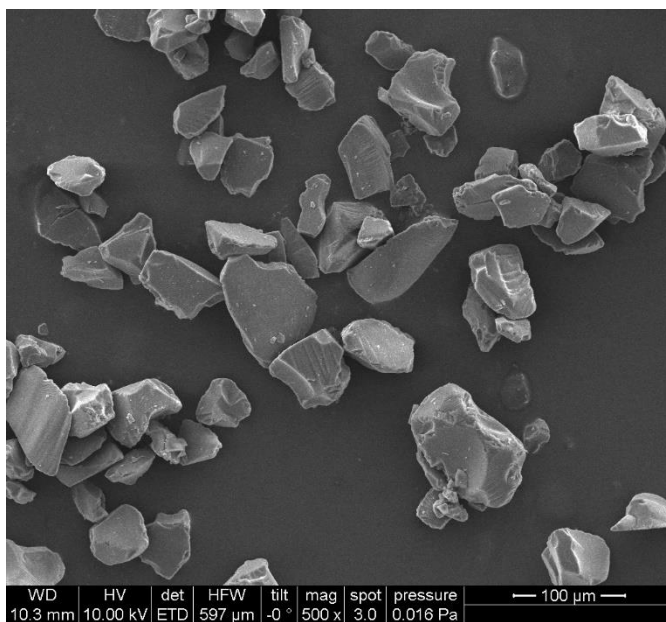


Figure S5 SEM image of PGM-loaded SILP with P₆₆₆₁₄Cl loading of 20% (w/w).

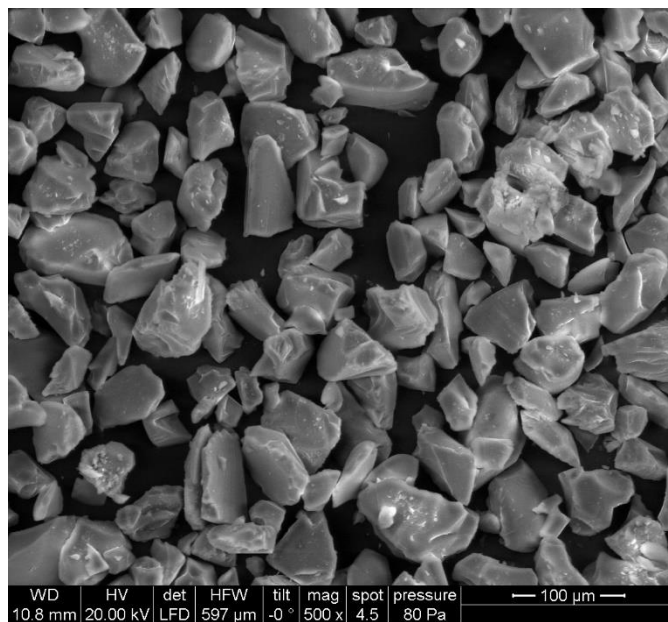


Figure S6 SEM image of polySILP with a loading of 20% (w/w).

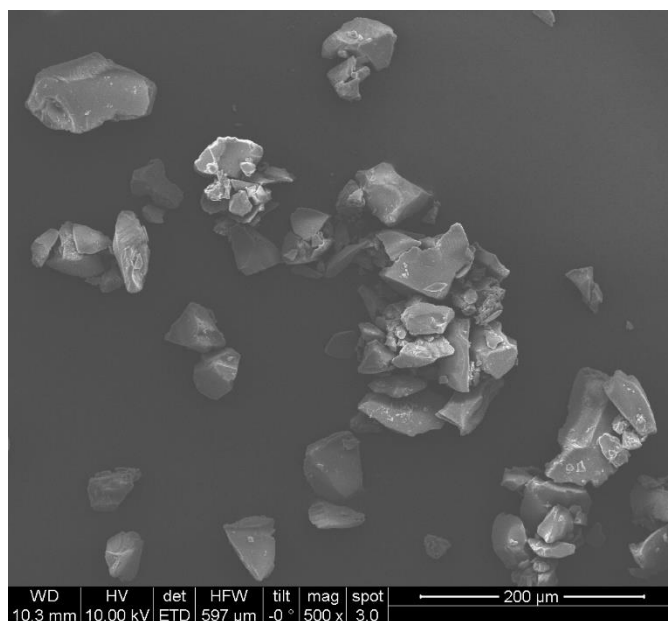


Figure S7 SEM image of PGM-loaded polySILP with a loading of 20% (w/w).

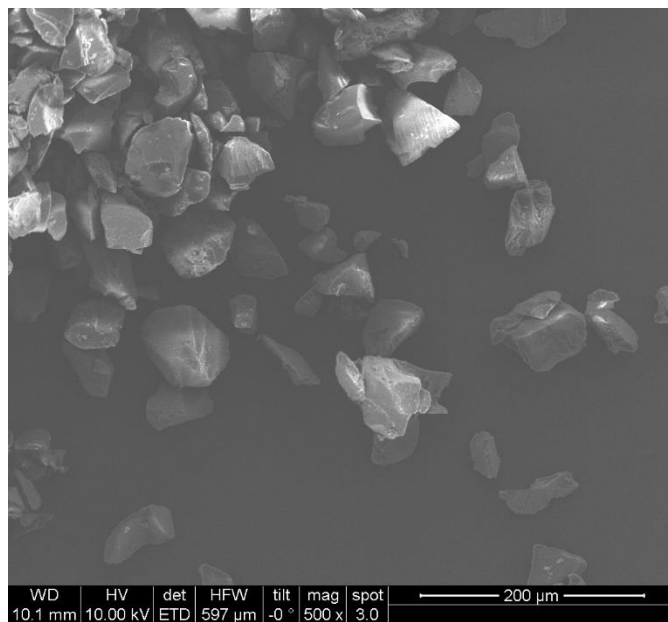


Figure S8 SEM image of polySILP with a loading of 20% (w/w) after stripping 1.

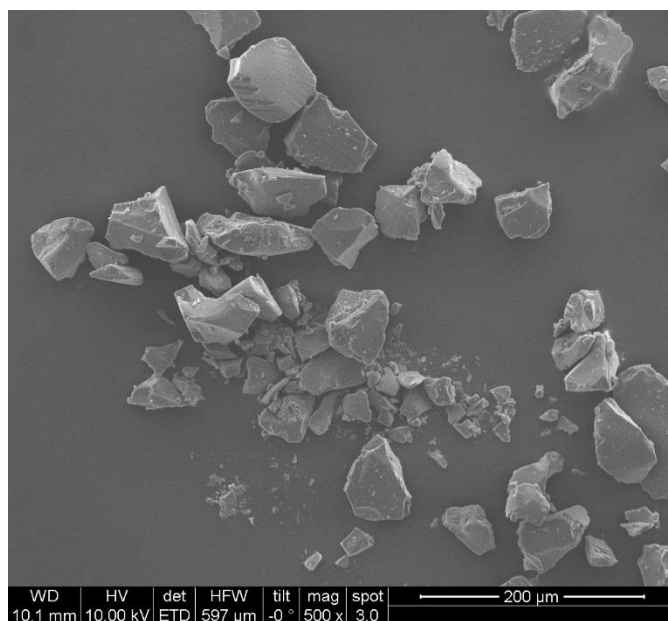


Figure S9 SEM image of polySILP with a loading of 20% (w/w) after stripping 2.

5. Retention of PGMs from model solutions on SILPs and polySILPs

Effect of HCl concentration

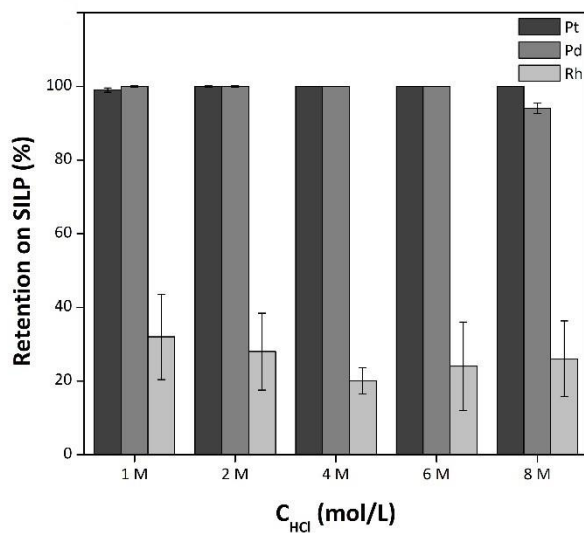


Figure S10 Effect of HCl concentration on PGM retention from model solution on SILP with $P_{66614}Cl$ loading of 10% (w/w).

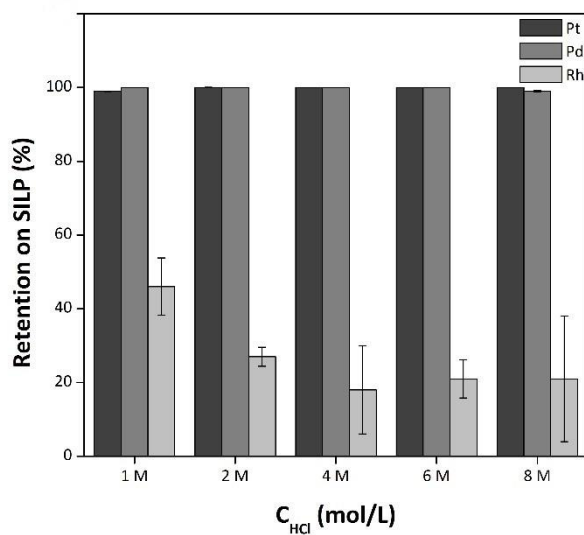


Figure S11 Effect of HCl concentration on PGM retention from model solution on SILP with $P_{66614}Cl$ loading of 20% (w/w).

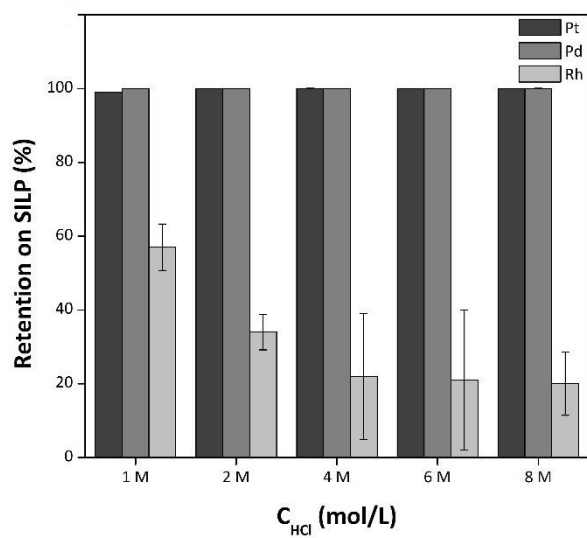


Figure S12 Effect of HCl concentration on PGM retention from model solution on SILP with $P_{66614}Cl$ loading of 50% (w/w).

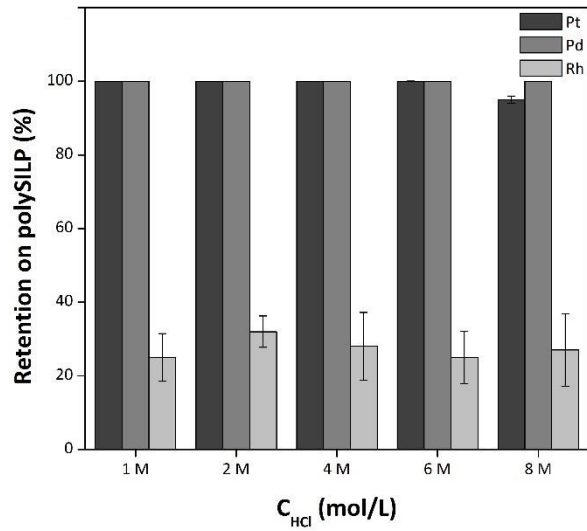


Figure S13 Effect of HCl concentration on PGM retention from model solution on polySILP with loading of 10% (w/w).

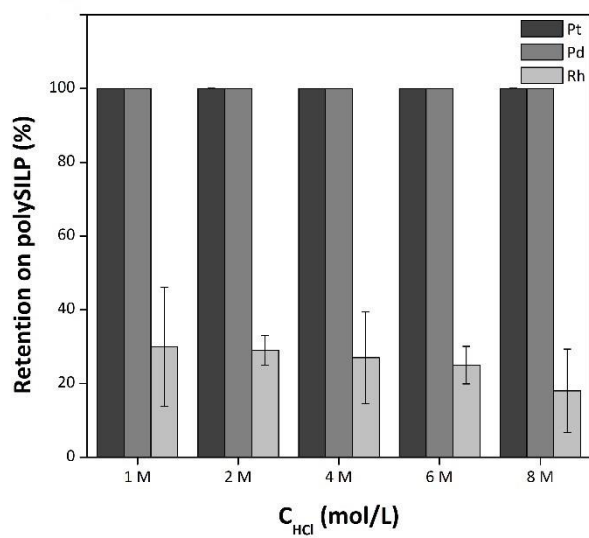


Figure S14 Effect of HCl concentration on PGM retention from model solution on polySILP with loading of 20% (w/w).

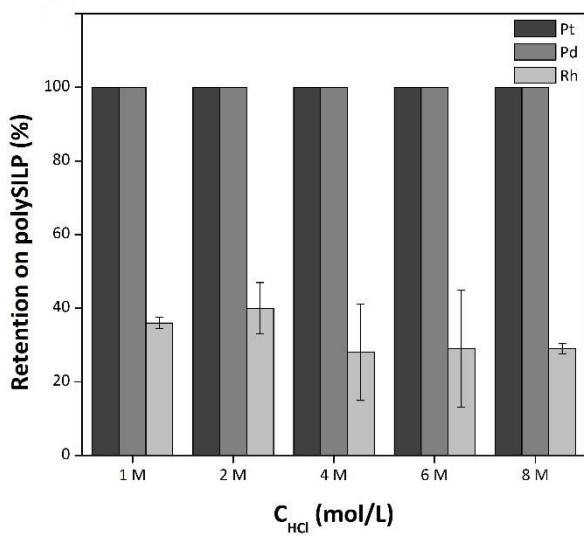


Figure S15 Effect of HCl concentration on PGM retention from model solution on polySILP with loading 50% (w/w).

Effect of dilution

The term “undiluted” refers to the model solution (194 ppm Pt, 318 ppm Pd and 34 ppm Rh) to contrast it with the different dilution levels.

The dilution was performed with H₂O on a X:Y ratio, where X refers to the model solution and Y to H₂O.

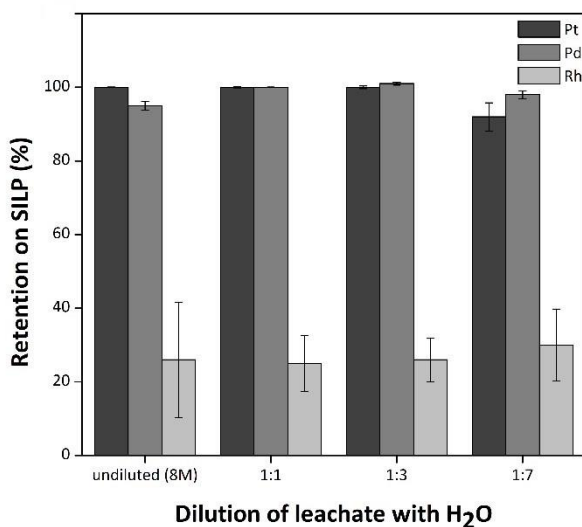


Figure S16 Effect of dilution PGM retention from model solution on SILP with P₆₆₆₁₄Cl loading of 10% (w/w).

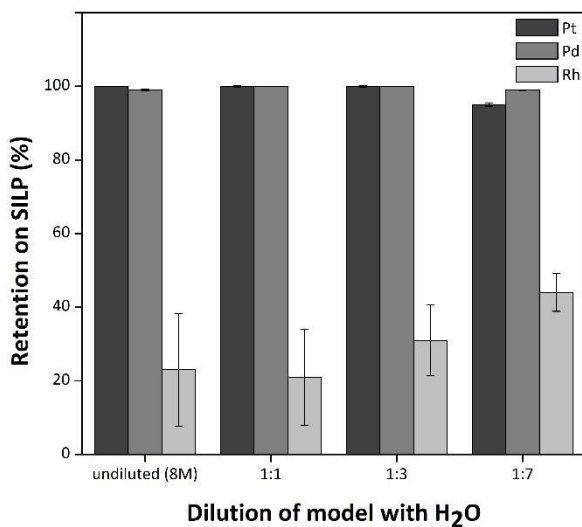


Figure S17 Effect of dilution on PGM retention from model solution on SILP with P₆₆₆₁₄Cl loading of 20% (w/w).

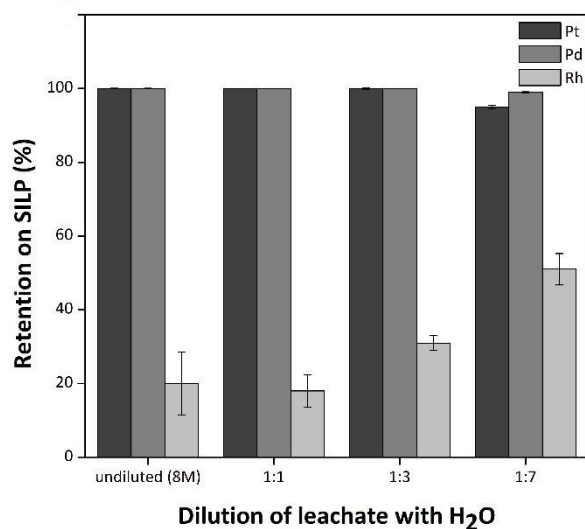


Figure S18 Effect dilution on PGM retention from model solution on SILP with P₆₆₆₁₄Cl loading of 50% (w/w).

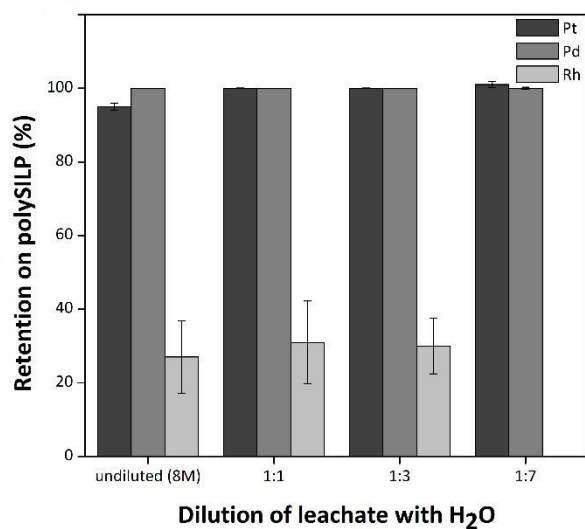


Figure S19 Effect of dilution on PGM retention from model solution on polySILP with loading of 10% (w/w).

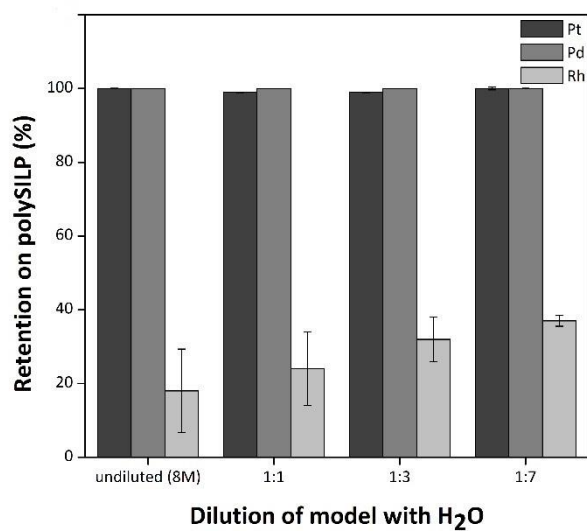


Figure S20 Effect of dilution on PGM retention from model solution on polySILP with loading of 20% (w/w).

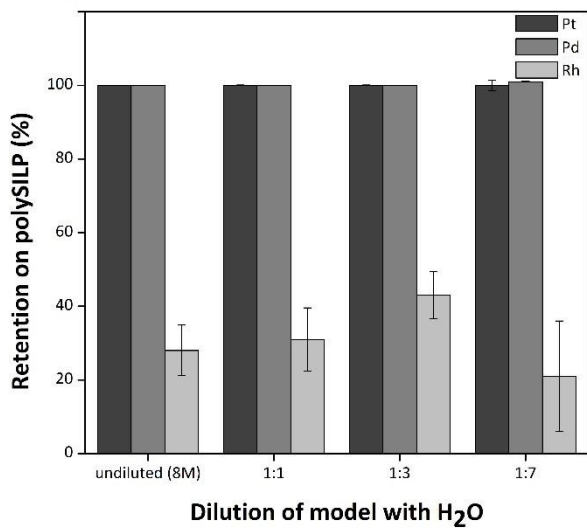


Figure S21 Effect of dilution on PGM retention from model solution on polySILP with loading of 50% (w/w).

Effect of ionic liquid loading on solid material

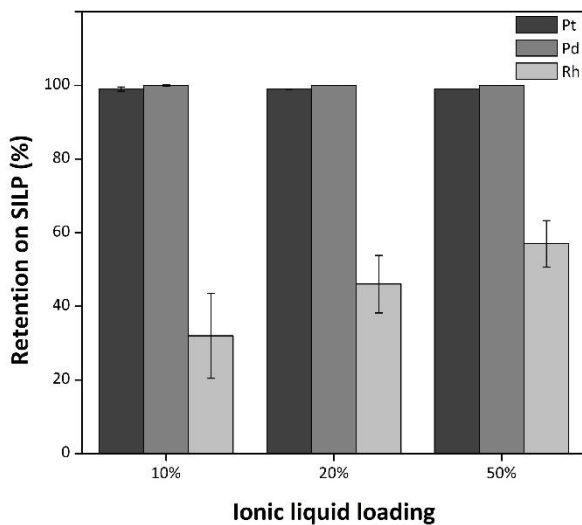


Figure S22 Effect of ionic liquid loading on SILP on PGM retention from 8M HCl model PGM solution diluted 1:7 with H₂O.

6. Retention of PGMs from real leachate on SILP 20% (w/w)

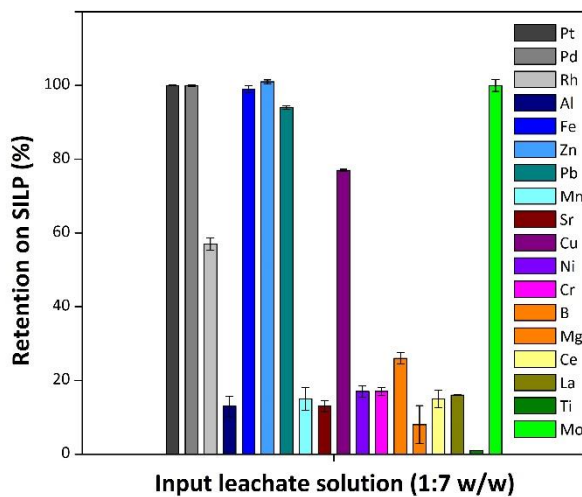


Figure S23 Retention behavior of PGMs and accompanying elements from automotive catalyst leachate on SILP 20% (w/w).

7. Retention of PGMs from real leachate on recycled polySILP 20% (w/w)

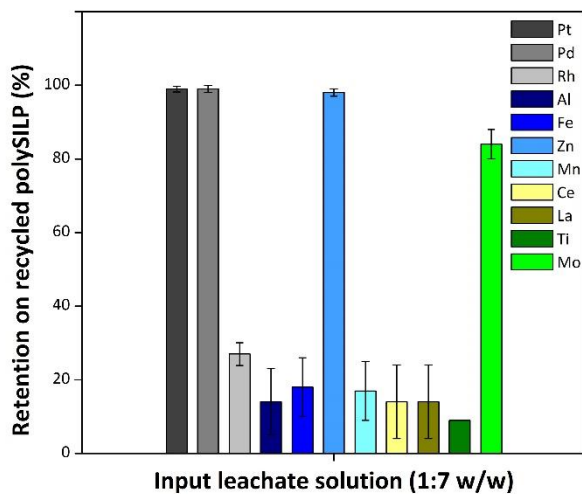


Figure S24 Retention behavior on recycled polySILP 20% (w/w).

8. Breakthrough curves for polySILP 20% (w/w) and Amberlite IRA-400

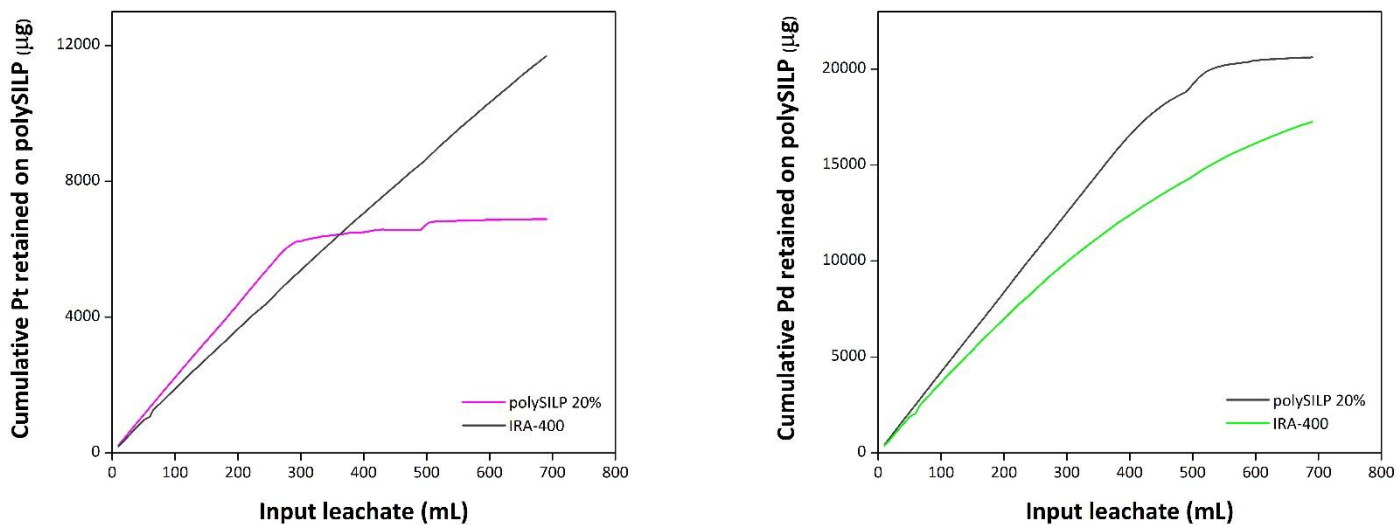


Figure S25 Breakthrough curves for Pt (left) and Pd (right) on polySILP 20% (w/w) and Amberlite IRA-400.

9. Characterization of car catalyst material

The spent car catalyst used in this study was fully characterized prior to the experiments (Table 1). It was digested with the aid of a mixture of mineral acids in a microwave oven (Multiwave 3000, Anton Paar, Germany), prior to measurement, for the complete dissolution of the ceramic material, which primarily comprises the car catalyst. The following digestion programme was employed; 8:00 at 500 W; hold 8:00; 15:00 at 900 W; hold 35:00. The quantification was performed by ICP-OES (Radial iCAP6500, Thermo Scientific, USA) with appropriate sample dilution. The fitness for purpose of the analytical measurement method was initially verified with the aid of the certified reference material ERM-EB504.

Table S1 Concentration of elements in car catalyst and acidic leachate

Elements	Solid catalyst (ppm)	Acidic leachate (ppm)
Pt	970 ± 20	150 ± 2
Pd	1590 ± 40	293 ± 4
Rh	343 ± 8	27 ± 0.4
Al	311740 ± 22722	3512 ± 38
Ce	27600 ± 1400	1176 ± 12
Fe	7096 ± 647	655 ± 8
Zn	4226 ± 574	269 ± 9
Sr	830 ± 225	297 ± 6
La	3857 ± 320	384 ± 4
Mg	7687 ± 309	1036 ± 14
Pb	463 ± 61	69 ± 5
Cu	154 ± 17	20 ± 0.4
Ni	278 ± 43	13 ± 0.6
Cr	262 ± 66	23 ± 0.2
Mn	247 ± 36	17 ± 0.3
Ba	3165 ± 770	4 ± 0.2
B	65 ± 10	10 ± 1
Ti	3170 ± 10	47 ± 1
Mo	82 ± 8	15 ± 0.2

10. ICP-OES measurement parameters

The PGM concentrations in all systems were quantified with a radial ICP-OES (Thermo iCAP 6500, Thermo Scientific, USA) with a sample introduction kit consisting of a parallel path nebulizer (PEEK Mira Mist, Thermo Scientific, Canada), a gas cyclonic spray chamber with a riser tube and a torch injector tube with 2 mm inner diameter. Signals in ICP-OES were recorded and processed using Qtegra 2.10 software (Thermo Scientific, USA).

Table S2 ICP-OES instrumental measurement parameters

Instrument	Radial iCAP 6500 (Thermo Scientific, USA)
Software	Qtegra 2.10 (Thermo Scientific, USA)
RF power	1400 W
Torch internal diameter	2.0 mm

Nebulizer	V-groove nebulizer (Thermo Scientific, USA)
Nebulizer gas flow	0.70 L/min
Coolant gas flow	12 L/min
Auxiliary gas flow	0.80 L/min
Sample introduction flow rate	0.70 mL/min
Viewing height	10 mm
Exposure time (in Vis)	10 sec
Observation time per measurement	5 sec
Number of replicates pre measurement	5

Table S3 Selected emission wavelengths for elemental quantification

Element	Quantification wavelength	Quality control wavelength
Pt	265.945	214.423
Pd	340.458	324.270
Rh	343.489	369.236
Al	309.271	237.312
Fe	259.940	238.204
Zn	213.856	202.548
Sr	407.771	421.552
Mg	279.553	280.270
Ca	315.887	318.128
Pb	220.353	216.999
Ce	456.236	380.152
Cu	324.754	327.396
Ni	221.647	231.604
Mn	257.610	293.930
Cr	267.716	-
Ba	455.403	-
B	249.773	249.678
Mo	202.030	-
La	261.034	-
Ti	334.941	308.802-