Electronic Supplementary Material (ESI) for ChemComm.

Dissolution of noble metals in highly concentrated acidic salt solutions

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Electronic supplementary information (ESI)

Chemicals

$AlCl_3{\cdot}6H_2O$ (>99%), $Al(NO_3)_3{\cdot}9H_2O$ (>98.5%), palladium (Pd) wires (99.9%, 0.5 mm diameter), gold (Au) wire (99.997%, 1 mm diameter) and ascorbic acid (≥99.0%) were purchased from Sigma-Aldrich (Steinheim, Germany). HCl (37 wt%) was obtained from VWR Chemicals (Leuven, Belgium), HNO_3 (65 wt%) and H_2O_2 (50 wt%) from Chem-Lab NV (Zedelgem, Belgium). HBF_4 (50 wt% in H_2O) was purchased Alfa Aesar (Kandel, Germany). The catalyst powder was kindly provided by Monolithos (Athens, Greece) with particle size < 0.2 mm. The standard solutions (1000 mg L^{-1} Pd, Pt, Rh, Al, Ce, Fe, Zn, Cd, Y) were obtained from Merck (Overijse, Belgium). Water was always of ultrapure quality, deionized to a resistivity of 18.2 MΩ cm with a Sartorius Arium® Pro ultrapure water system. All chemicals were used as received without any further purification.

Analytical techniques

Metal concentrations in the aqueous phase were determined by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) using a Perkin-Elmer Avio® 500 instrument. Calibration curves were constructed by preparing, in 5 vol% HCl, solutions of: 0.5-5 mg L^{-1} Pt, Pd and Rh, 5–50 mg L^{-1} Al, Ce and 0.5-10 mg L^{-1} Fe, Zn; 1000 mg L^{-1} cadmium and yttrium standard solutions were then added and used as internal standards. The following spectroscopic lines were used: Pt 265.945 nm, Pd 363.470 and 340.458 nm, Rh 343.489 nm, Al 396.153 nm, Ce 413.764 nm, Fe 238.204 nm and Zn 206.200 nm.

Characterization

The platinum-group metals content in the catalyst powder was determined by microwave digestion (Speedwave Xpert, Berghof) followed by ICP-OES analysis. Samples (100 mg) were treated with the following acid mixture: 5 mL HCl 37 wt% + 4 mL HNO_3 65 wt% + 3 mL HBF_4 50 wt% + 3 mL H_2O_2 35 wt% in 100 DAK vessels and using the digestion method reported in Table S1. Digestion tests were performed in triplicate. Samples were quantitatively transferred from the vessels to volumetric flasks using 37 wt% HCl, then diluted accordingly with 5% HCl and analyzed with ICP-OES.

Leaching

Leaching tests were performed by contacting the solid material (wire/catalyst powder) in glass vials located on a stirring plated equipped with aluminium block and a temperature probe (T = 80 °C, stirring speed = 350 rpm). Several operative parameters were tested, such as the salt-to-catalyst ratio (S/C ratio), the contact time and the water content. After leaching, the solid material was separated from the leachate by vacuum-filtration while washing with water. The obtained solution was transferred into volumetric flasks (100 mL) and further filtrated through a syringe filter with a pore size of 0.45 μm, prior to ICP-OES analysis. The leaching efficiency $E_L(\%)$ was determined according to eqn 1:

$$\mathrm{E_L(\%)} = \frac{\mathrm{m_L}}{\mathrm{m_0}} \times 100 \tag{1}$$

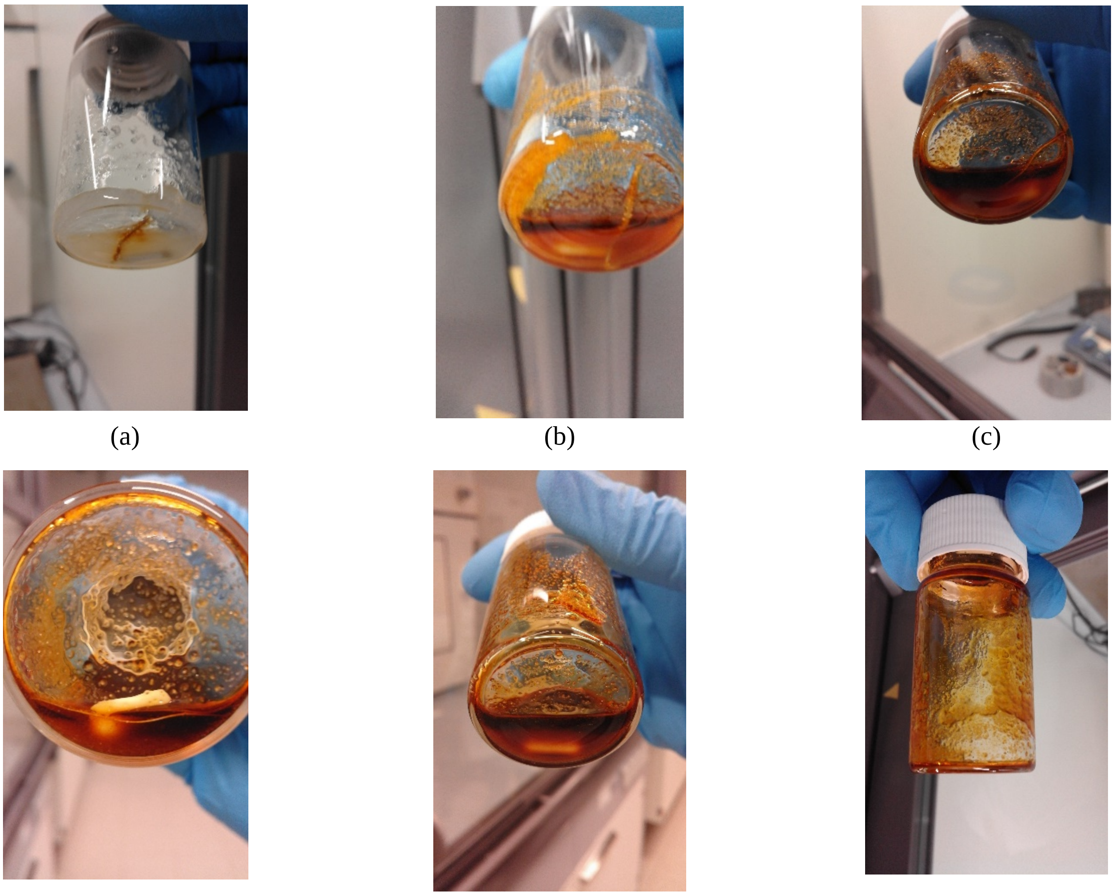
where m_L is the mass of the dissolved metal (mg) and m_0 is the mass of metal in the initial sample (mg).

Precipitation

PGM recovery was investigated by reductive precipitation with ascorbic acid. Precipitation tests were performed by contacting the leachate with solutions of ascorbic acid in water in plastic vials located on a mechanical shaker (TMS-200 Turbo Thermoshaker, 2500 rpm, 5 min). Several concentration of ascorbic acid were tested. Samples were then centrifuged (3500 rpm, 5 min) to separate the solid residue from the aqueous phase; the latter was analyzed *via* ICP-OES to determine the precipitation efficiency E_P, defined as in eqn 2:

$$\mathrm{E_P(\%)} = \frac{\mathrm{m_P}}{\mathrm{m_L}} \times 100 = \frac{\mathrm{m_L} - \mathrm{m_R}}{\mathrm{m_L}} \times 100 \tag{2}$$

where m_P is the mass of metal precipitated (mg) and m_R is the remaining mass of metal in the leachate after precipitation (mg).



(a) (b) (c)

(d) (e) (f)

Figure S1: Palladium wire in contact with the molten salt hydrate mixture, after 3 min (a), 1 h (b), 2 h (c), 3 h (d), 4 h (e) and 4.5 h (f) leaching; S/C ratio = 35 g/g, T = 80 °C, water added = 22 wt%, stirring speed = 350 rpm.

(a) (b) (c)

Figure S2: Gold wire in contact with the molten salt hydrate mixture after 3 h (a), 5 h (b) and 24 h (c) leaching; salt-to-wire (S/W) ratio = 35 g/g, T = 80 °C, water added = 22 wt%, stirring speed = 350 rpm.

Table S1. Digestion method for the characterization of the spent automotive catalysts.

T, °C	P, bar	Ramp time, min	Holding time, min	P, %
170	60	8	8	27
200	60	15	35	50
50	60	1	5	0
50	40	0	0	0
50	40	0	0	0

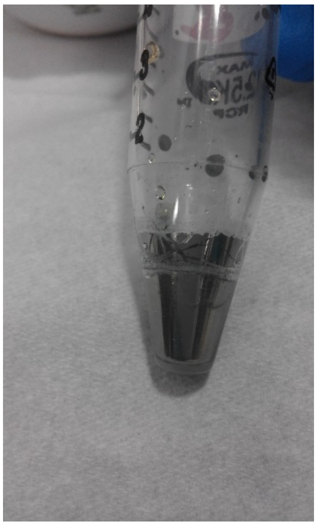


Figure S3: Reductive precipitation of palladium with ascorbic acid solution in water (T = 25 °C, 1 mol L^{-1} ascorbic acid).