



Research article

The pH-dependent release of platinum group elements (PGEs) from gasoline and diesel fuel catalysts: Implication for weathering in soils

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ABSTRACT

Powdered samples of new and old gasoline catalysts (Pt, Pd, Rh) and new and old diesel (Pt) catalysts were subjected to a pH-static leaching procedure (pH 2–9) coupled with thermodynamic modeling using PHREEQC-3 to verify the release and mobility of PGEs (platinum group elements). PGEs were released under acidic conditions, mostly exhibiting L-shaped leaching patterns: diesel old: 5.47, 0.005, 0.02; diesel new: 68.5, 0.23, 0.11; gasoline old: 0.1, 11.8, 4.79; gasoline new 2.6, 25.2, 35.9 in mg kg⁻¹ for Pt, Pd and Rh, respectively. Only the new diesel catalyst had a strikingly different leaching pattern with elevated concentrations at pH 4, probably influenced by the dissolution of the catalyst carrier and washcoat. The pH-static experiment coupled with thermodynamic modeling was found to be an effective instrument for understanding the leaching behavior of PGEs under various environmental conditions, and indicated that charged Pt and Rh species may be adsorbed on the negatively charged surface of kaolinite or Mn oxides in the soil system, whereas uncharged Pd and Rh species may remain mobile in soil solutions.

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1. Introduction

Motor vehicle emissions are one of the key contributors to the presence of precious metals, such as platinum group elements (PGEs), in an urban environment (Ravindra et al., 2004). In the 1970s in the U.S.A. and later in Europe, automobile exhaust catalysts were first introduced to control and limit pollutants such as CO, NO_x and hydrocarbons. PGEs are used due to their high catalytic activities for controlling exhaust emissions and they are also less prone to poisoning and high-temperature deactivation than other metals (Heck et al., 2012). The catalysts wear down chemically and physically during operation as a consequence of a change in the redox conditions, high temperature and mechanical abrasion. As a result, PGEs can be emitted with the exhaust gases in inert and soluble particle form (Moldovan et al., 2002; Palacios et al., 2000; Zereini et al., 1997). The emitted particles settle into the environment and can migrate. The release of PGEs has given rise to elevated concentrations in road and tunnel dusts, soils, sediments and water (Ravindra et al., 2004 and references therein). Moldovan et al. (2002) observed that small quantities of PGEs, of the order of

55–120 ng km⁻¹ and 2–9 ng km⁻¹ for fresh and aged gasoline catalysts, and 82 ng km⁻¹ and 130 ng km⁻¹ for Pt-based fresh and aged diesel catalysts, respectively, are released and deposited along a roadside environment during simulated driving conditions.

In addition, PGEs can bioaccumulate in food chains (Haus et al., 2007; Marcheselli et al., 2010) and are suspected of having harmful effects on the environment and human health (Apostoli et al., 2006).

Understanding the leaching characteristics has important ecotoxicological relevancy. Leaching tests can be used to obtain information about contaminant leachability and solubility-controlling phases. The pH is one of the key parameters controlling the leaching process. So far, pH-static leaching tests have been used to assess the pH-dependent leaching behavior of metals in different types of matrices: contaminated soils and slags (Van Herreweghe et al., 2002; Vítková et al., 2011), fly ash and bottom ash from waste incinerators (Dijkstra et al., 2006), fly ash from lead or cobalt smelters (Vítková et al., 2013, 2009) or building material such as bricks (Karius and Hamer, 2001), but never for dust from fuel catalysts.

The present paper is focused on assessment of the pH-dependent leaching from various catalysts with special emphasis on PGEs and comparison of the leaching behavior of new and aged gasoline and diesel catalysts.

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2. Materials and methods

2.1. Catalysts' samples

About 500 g of dust samples were mechanically separated from four automotive catalytic converters and prepared by grinding in an agate mill and drying at 105 °C to constant weight. Two gasoline and two diesel catalysts designed for Škoda Octavia vehicles (ŠKODA AUTO, Czech Republic, Member of the Volkswagen Group) were used for the leaching experiments. A new Škoda Octavia 1.8 L (motor code MG8, 110 kW, emission level EU 4) gasoline catalyst (gasoline new, denoted hereafter as GN) was obtained and the technical documentation states that the whole catalytic converter contains ~ 0.269 g Pt, 4.301 g Pd and 0.269 g Rh. The carrier of the catalytic layer is made of metal with dimensions of 118 mm × 174 mm (diameter × length) and has a volume of approx. 1903 cm³. An identical catalyst from a vehicle which had travelled 100,000 km was also used for the experiment and denoted as GO: gasoline old. A Škoda Octavia 1.9 L (motor code MNO, 81 kW TDI, emission level EU 3) diesel catalytic converter was obtained. The carrier of the catalytic layer is a ceramic monolith with dimensions of 118 mm × 152 mm (diameter × length) and a volume of 1678 cm³, containing at least 1.343 g of Pt; other PGEs were not reported in the technical documentation. An identical catalyst was acquired from a vehicle that had travelled 100,000 km (diesel old – DO). In addition, ground synthetic cordierite (České lupkové závody a.s., Czech Republic) was used for experiments to simulate leaching of the honeycomb matrix of the diesel catalysts. The mineralogical compositions of the individual catalysts and synthetic cordierite were determined using X-ray diffraction analysis (XRD) performed with a PANanalytical X'Pert Pro diffractometer equipped with a secondary monochromator and X'Celerator multichannel detector (conditions: Cu K α radiation, 40 kV, 30 mA, range 5–80° 2 θ , step 0.02°, counting time 300 s per step). The chemical compositions were determined by inductively coupled plasma – optical emission spectrometry (ICP-OES; iCAP 6500, Thermoscientific) following mineralisation with a mixture of HF and HClO₄ acids. The contents of the PGEs were determined by inductively coupled plasma –

mass spectrometry (ICP-MS, XSeries 2, Thermoscientific) after dokimastic separation into NiS (analytical details are given in Šebek et al., 2011). The mineralogical and chemical compositions of the catalysts are listed in Table 1.

2.2. pH-static leaching test

All of the catalyst samples were subjected to the pH-static leaching test according to European standard CEN/TS 14997 (2006). All the experiments were performed in duplicate and with procedural blanks at room temperature for 48 h. An amount of 2 g of the catalyst sample was placed in 50-ml polypropylene centrifuge tubes (Thermoscientific). Then 19 ml of MilliQ + deionised (DI) water were added to maintain an L/S ratio of 9 with a final L/S ratio of 10 after addition of the acid/base. Eight pH-static set points were predefined (pH 2, 3, 4, 5, 6, 7, 8 and 9) to cover various environmental conditions. Either acid (1 and 14 M HNO₃) or base (1, 2 and 5 M NaOH) was added depending on the set-point pH. The pH set points were continuously adjusted by addition of weaker acid/base. All the catalysts were leached at their natural pH. The reactors were constantly agitated using a horizontal shaker. After 48 h, the reactors were centrifuged to settle suspended particles and the leachate was filtered through 0.45 μ m membrane filters (Millipore, USA). The physico-chemical parameters (pH, Eh and conductivity) were recorded after the end of experiment measured using Schott multimeters (Schott, Germany). The same methodology was used for the dissolution of synthetic cordierite and also DN with smaller steps in the pH-range 2–5.5 to investigate the leaching of PGEs and the major elements (see reasoning below).

2.3. Leachate analyses

The leachates from each experiment were analyzed for platinum group elements (Pt, Pd and Rh) and other metals (Al, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, La, Ce, Pb) using ICP-MS (XSeries 2, Thermoscientific) and ICP-OES (Varian Vista MPX, Australia). Anions were determined only in the DI water leachate (L/S = 10) by high-performance liquid chromatography (HPLC ICS-2000, AS50 autosampler, ionic column IonPac AS 18 analytical, Dionex). The accuracy of the analyses was controlled using a SRM 2556 – Recycled Pellet (Autocatalyst-NIST USA) standard reference material. The accuracy of the determination of PGEs was within 5% of the relative standard deviation (RSD).

2.4. Data treatment

The calculation of species in the leachates and determination of the solubility-controlling phases were carried out in PHREEQC-3 (Parkhurst and Appelo, 2013) equipped with the LNLL database (Delany and Lundeen, 1990). The database was extended by additional data taken from the literature (Azaroual et al., 2001; Byrne and Yao, 2000; Elding, 1978; Forrester and Ayres, 1959; Hartley, 1991; Maslei et al., 1976; Nabivanets and Kalabina, 1970; Sassani and Shock, 1998; Wagman et al., 1982). The program was used to calculate the Pt(II), Pd(II) and Rh(III) species. Rhodium(III) is the most common oxidation state in aqueous solution. Platinum and Pd can occur in either the (II) or (IV) valence state but the divalent state largely predominates over the tetravalent state at 25 °C except under very oxidizing conditions (Hartley, 1991).

Table 1
Elemental and phase compositions and pHz_{pc} of the catalysts (according to Šebek et al., 2011).

| | | GO | GN | DO | DN |
|-------------------|---------------------|--------|--------|----------|---------|
| Al | % | 28.3 | 27.0 | 17.6 | 21.4 |
| SiO ₂ | % | 0.40 | <0.1 | 41.2 | 41.3 |
| C tot | % | 0.42 | 0.84 | 0.39 | 0.07 |
| S tot | % | 0.61 | 0.01 | 1.51 | <0.1 |
| Mg | mg kg ⁻¹ | 445 | 7.70 | 47,900 | 56,600 |
| Fe | mg kg ⁻¹ | 15,000 | 10,900 | 3350 | 2800 |
| Ti | mg kg ⁻¹ | 626 | 607 | 2810 | 2730 |
| K | mg kg ⁻¹ | 79.3 | 48.0 | 200 | 233 |
| Na | mg kg ⁻¹ | 155 | 92.6 | 949 | 591 |
| Ca | mg kg ⁻¹ | 465 | <2 | 320 | 167 |
| Mn | mg kg ⁻¹ | 313 | 31.5 | 16.5 | 14.0 |
| Zr | mg kg ⁻¹ | 35,000 | 33,400 | 59.0 | 234 |
| Ce | mg kg ⁻¹ | 79,600 | 90,000 | 32.0 | 109 |
| Pt | mg kg ⁻¹ | 679 | 763 | 3980 | 3850 |
| Pd | mg kg ⁻¹ | 11,500 | 10,300 | <0.5 | <0.5 |
| Rh | mg kg ⁻¹ | 702 | 777 | <0.1 | <0.1 |
| Pd/Pt | | 17.0 | 13.5 | 0.000126 | 0.00013 |
| Pd/Rh | | 16.4 | 13.3 | | |
| Cordierite | | | | xxxx | xxxx |
| Al oxide | | xxxx | xxxx | | |
| Ce oxide | | xxxx | xxxx | | |
| pHz _{pc} | | 8.35 | 8.01 | 3.82 | 6.34 |

Abbreviations: DO – diesel old, DN – diesel new, GO – gasoline old, GN – gasoline new

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