Dissolution kinetics of Pd and Pt from automobile catalysts by naturally occurring complexing agents

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ABSTRACT

Powder samples prepared from gasoline (Pt, Pd, Rh, new GN/old GO) and diesel (Pt, new DN/old DO) catalysts and recycled catalyst NIST 2556 were tested using kinetic leaching experiments following 1, 12, 24, 48, 168, 360, 720 and 1440-h interactions with solutions of 20 mM citric acid (CA), 20 mM $Na_2P_4O_7$ (NaPyr), $1 g L^{-1}$ NaCl (NaCl), a fulvic acid solution (FA–DOC $50 mg L^{-1}$) and 20 mM CA at pH 3, 4, 5, 6, 7, 8 and 9. The mobilisation of platinum group elements (PGEs) was fastest in solutions of CA and NaPyr. In the other interactions (NaCl, FA), the release of PGEs was probably followed by immobilisation processes, and the interactions were not found to correspond to the simple release of PGEs into solution. Because of their low concentrations, the individual complexing agents did not have any effect on the speciation of Pd and Pt in the extracts; both metals are present in solution as the complexes $Me(OH)_2$, $Me(OH)^+$. Immobilisation can take place through the adsorption of the positively charged hydroxyl complexes or flocculation of fulvic acid, complexing the PGEs on the surface of the extracted catalysts. The calculated normalised bulk released NRi values are similar to the reaction rate highest in the solutions of CA and NaPyr.

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1. Introduction

Platinum group elements (PGEs), especially platinum (Pt), palladium (Pd) and rhodium (Rh), are most carefully recycled in cases where they are used by humans. They are generally considered to be inert metals with low mobility [1]. When they are used as automobile catalysts, substantial amounts of these metals are emitted into the environment [2–4]. Emitted PGEs accumulate in the media around roadways, especially in soils or fluvial systems draining water from the surface of the roadways [5]. Most of the emitted PGEs occur in the form of particles with a size and in an amount that is dependent particularly on the state of the catalyst [6]. The particles consist mainly of metals and possibly also oxides; a portion of PGEs is emitted in automobile exhaust in the water-soluble fraction [7]. The water-soluble forms are assumed to be chloro-complexes and organo-complexes with carbonyl [8].

In an exogenic environment, the catalyst particles of PGEs can be solubilised and, as a final consequence, could enter the food chain [9]. The solubility and mobility of the individual PGEs are dependent on the pH and the ability of the individual Pt metals to form neutral or charged inorganic and organic complexes. Organic material plays an important role in the mobilisation and immobilisation of PGEs [10]. Organic substances in the exogenic environment can (i) form soluble complexes with PGEs, (ii) reduce the soluble forms of metals and cause their precipitation and (iii) adsorb the metals [11]. Citrates are common low-molecular weight (LMW) organic substances contained in root exudates. They affect the weathering of minerals in artificial phases and, as a consequence, the mobility of nutrients and toxic substances [12]. The mobilisation of PGEs into solution also occurs though the effect of inorganic ligands, especially phosphates, chlorides and cyanides [13,14].

Most of the published works related to the mobilisation of PGEs are concerned with the soil and sediments in the vicinity of roadways, road dust [15–17] and geochemical archives [18,19] or describe experiments with metallic Pt or platinum black and Pt compounds [20,21].

The present study was performed to elucidate the processes affecting the rate of dissolution of particles from gasoline or diesel fuel catalysts in solutions of ligands complexing PGEs in media with different pH values, which could occur in forests, agricultural

soils or soils close to roadways. These substances are derived from agricultural activities (PO_4), are contained in melt waters after the chemical treatment of roadways in the winter (NaCl), occur in soils as products of the functioning of the rhizosphere (citric acid) or are stable natural products of the transformation of cellulose or lignin (fulvic acid).

2. Materials and methods

2.1. Solid samples

Two gasoline and two diesel fuel catalysts (old and new) were used for the batch experiments. The gasoline catalyst (gasoline new – GN) Škoda Octavia 1.8 L (motor code MG8, 110 kW, emission level EU 4) contains approx. 0.269 g Pt, 4.301 g Pd and 0.269 g Rh. The carrier is twisted metal with dimensions of 118 mm × 174 mm (diameter × length) and a volume of approx. 1903 cm^3. An identical catalyst from a vehicle that had travelled 100,000 km was also used (gasoline old – GO). The diesel catalyst (diesel new – DN) was obtained from the motor of a Škoda Octavia (1.9 L 81 kW TDI, motor code MNO, emission level EU 3). The carrier is a ceramic monolith with dimensions of 118 mm × 152 mm (diameter × length) and a volume of 1678 cm^3, containing at least 1.343 g of Pt. The same catalyst was also obtained from a motor that had travelled 100,000 km (diesel old – DO). Approx. 500 g of dust was prepared from each of the catalysts; this was ground on an agate mill, dried in a dry box at 105 °C to a constant weight and used for further experiments. Leaching was simultaneously performed with standard reference material SRM 2556 (Used Autocatalyst – Pellets, NIST USA). The specific surface area of the studied samples was determined by three-point N_2 BET surface measurement (Sorptomatic 1990, Carlo Erba, Instruments, UK). The main phases of the individual catalysts 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. The analyses were performed under the following conditions: CuKα radiation, 40 kV, 30 mA, scan in steps of 0.02°/250 in the range 3–80° 2 theta. The surface, morphology and composition of the individual samples were studied using a CamScan scanning electron microscope equipped with an EDS Link ISIS 300 microanalytical system.

The elemental composition of the catalysts was determined by ICP OES (iCAP 6500, Thermoscientific). The determination was performed following mineralisation of the samples with a mixture of acids, HF and $HClO_4$. The contents of Pt, Pd, Rh and Ru were determined using ICP MS following docimastic separation into NiS [19]. The compositions of the prepared solutions were measured by inductively coupled plasma mass spectrometry (ICP MS, X Series 2, Thermoscientific) under the conditions given in the Strnad et al. [19]. The quality of the analytical measurement was controlled using the standard reference materials NIST 2556, WMG-1 (Mineralized Gabro, CCRMP Canada) and UMT-1 (Ultramafic Ore Tailings PGE Reference Materials, CCRMP Canada).

2.2. Batch experiments

2.2.1. Leaching solutions
The following solutions were prepared for the leaching:

(i) Citric acid (CA) solution, 20 mM ($C_6H_8O_7$, Merck Germany, Mr 192.13 g mol^{-1}). Citric acid is a low molecular weight (LMW) organic acid whose concentration in organic-rich soil varies between 1 and 600 mM and that shows elevated levels particularly in soils containing normal fungus cultures [12,22,23].

(ii) Sodium pyrophosphate (NaPyr) solution, 20 mM ($Na_4P_2O_7$·10 H_2O, Sigma Aldrich, Mr 446.06 g mol^{-1}). Lustig et al. [13] describe the interaction of 0.2 M NaPyr with tunnel dust as a process of formation of a bidental complex in which up to 8% of the total Pt content in the dust particles can be mobilised.

(iii) Sodium chloride (NaCl) solution, 1 g L^{-1}. Particularly in acidic medium, chloride ions form soluble complexes with Pt and Pd [24]. The NaCl concentration in soil water in the vicinity of salted roadways sometimes exceeds a value of 1 g L^{-1} [25].

(iv) Fulvic acid solution (FA) was prepared from the Suwannee River fulvic acid standard (SRFAS, no. 1S101F, International Humic Substances Society, USA). The resulting content of soluble organic carbon (SOC) in the FA was 50.4 mg L^{-1}. High molecular weight (HMW) organic solutions such as FA play an important role in the mobilisation and transport of PGEs [10].

All the solutions were prepared in deionised water from a Millipore® Academic purifying system (Millipore, USA). Solution preparation and dilution were performed using analytical grade HNO_3 and HCl (Merck, Germany), which were additionally purified by sub-boiling distillation.

2.2.2. Leaching procedure with different complexing media
The batch leaching experiments were performed in 50 ml Falcon centrifugal vessels washed with acid. A total of 0.2 g of sample was weighed into each vessel, and 20 ml of leaching reagent was added. The reactors were carefully shaken in an end-over-end shaker (60 revs min^{-1}) at a temperature of 22 ± 3 °C. The individual reactors were prepared for time intervals of 1, 12, 24, 48, 168, 360, 720 and 1440 h. The reactors were wrapped in Al foil to prevent photo-oxidation of the organic acids. The experiments were performed in duplicate.

2.2.3. Extraction by citric acid at a different pH
A batch extraction experiment was performed with a solution of 20 mM CA buffered with a NaOH solution to a pH of approximately 3, 4, 5, 6, 7, 8 and 9. The experiments were performed with 0.2 g of GO catalyst (in relation to its Pd and Pt contents) by shaking (60 rpm) at a temperature of 22 ± 3 °C. The individual reactors were prepared for time intervals of 1, 4, 24, 48 and 168 h. The reactors were wrapped in Al foil to prevent photo-oxidation of the organic acids. The experiments were performed in duplicate.

2.2.4. Leachate analyses
The leachates were separated into two parts immediately after opening the reactors. The pH, Eh, specific conductivity and temperature were measured in one part of the leachate. The pH and Eh values were measured using a Schott-Geräte Handylab 1 pH meter equipped with a Schott L 7137 A combined electrode and a Schott PT 737 A redox electrode. The temperature and specific conductivity were determined using a Schott-Geräte Handylab 1 conductometer equipped with a LF 513 T measuring cell and a temperature detector. The second part of the leachate was centrifuged for 10 min at approx. 2000g. Subsequently, the supernatant was filtered through a 0.45 μm membrane filter (Millipore®) and acidified using 5% HCl. The acidification was not performed for the FA solution to prevent precipitation of the acid at low pH values. Platinum and Pd were determined using the standard configuration of a quadrupole-based inductively coupled plasma mass spectrometer (ICP MS, X-Series II, Thermo Scientific). The ICP MS data were acquired under the following conditions: measuring mode peak jump; 3 points per peak; instrument sensitivity 6×10^4 cps per 1 ng mL^{-1} ^{205}Tl; measured isotopes ^{108}Pd, ^{195}Pt, ^{198}Pt; internal standards ^{115}In, ^{205}Tl; total acquisition time 3 × 30 s; oxide formation (^{140}Ce^{16}O$^+$/^{140}Ce$^+$) less than 0.01. The Ar flow rates and

Table 1
Elemental and phase composition of the leached catalysts and NIST 2556 standard.

		GO	GN	DO	DN	NIST 2556
Al	%	28.30	27.01	17.62	21.40	44.77
SiO$_2$	%	0.4	<0.1	41.2	41.32	<0.1
C tot	%	0.42	0.84	0.39	0.07	0.53
S tot	%	0.61	0.01	1.51	<0.1	0.35
Mg	mg kg^{-1}	445	7.7	47,943	56,638	316
Fe	mg kg^{-1}	15,000	10,850	3350	2800	8250
Ti	mg kg^{-1}	625.92	606.77	2811	2733	50.77
K	mg kg^{-1}	79.3	48.0	200	233	160
Na	mg kg^{-1}	1548	92.6	949	591	912
Ca	mg kg^{-1}	465	<2	320	167	650
Mn	mg kg^{-1}	312.5	31.5	16.5	14	560
Zr	mg kg^{-1}	34,962	33,442	59	234	255
Ce	mg kg^{-1}	79,642	89,999	32	109	10,530
Pt	mg kg^{-1}	679	763	3975	3851	647
Pd	mg kg^{-1}	11,510	10,335	<0.5	<0.5	318
Rh	mg kg^{-1}	702	777	<0.1	<0.1	46
Pd/Pt		17.0	13.5	0.000126	0.00013	0.49
Pd/Rh		16.4	13.3			6.91
Cordierite				XXXX	XXXX	
Al oxide		XXXX	XXXX			
Corundum						XXX
Al$_2$O$_3$ monoclinic						XXXX
Ce oxide		XXXX	XXXX			

Relative abundance: XXXX – major, XXX – common.

parameters of the ionic optics were selected in relation to the maximum sensitivity and minimum oxide formation. The three-point calibration curve (blank, 25 ng mL^{-1}, 50 ng mL^{-1}) was prepared using Aristar (BDH Laboratory Supplies, UK) calibration solution. For comparison of the effect of other possible polyatomic interferences (^{89}Y^{16}O$^+$, ^{92}Zr^{16}O$^+$, ^{40}Ar^{65}Cu$^+$, ^{180}Hf^{18}O$^+$), part of the samples of all the obtained leachates was measured using a high resolution ICP MS (Element II, Thermo Bremen). In relation to the high concentrations of the leached Pt metals, the Pd and Pt concentrations exhibited very good agreement with the concentrations determined by the two analytical techniques (Pd: $R^2 = 0.9965$; Pt: $R^2 = 0.9811$).

2.3. Data treatment

Speciation-solubility modelling was performed using the PHREEQC-2 geochemical code, version 2.17 for Windows [26]. The SIT.dat thermodynamic database (derived ThermoChimie v.7.b database and implemented into the PHREEQC code in September 2010) was used for all the calculations. This database, which already contains some complexation data for Pd, was amended with the selected thermodynamic data for Pt complexation with chloride and hydroxide ions and Pd complexation with citrate from the NIST SRD 46 database [27] and related publications [28–30]. Unfortunately, no data for Pt and Pd complexation with pyrophosphate and FA are currently available in the literature. Data from the interactions after 1 and 1440 h were used for the modelling.

3. Results and discussion

3.1. Phase and chemical compositions of the studied catalysts

The phase and chemical compositions of the leached phases are given in Table 1. On the predominant phase on the monolithic gasoline catalyst formed of coiled metal, the following compounds were identified as the predominant phases of the active layer employed in the experiments: aluminium oxide (28.3 wt% Al in GO and 27.01 wt% in GN) and Ce oxide (7.96 wt% Ce in GO and 8.99 wt% in GN). Cordierite ($Mg_2Al_4Si_5O_{18}$), with the corresponding contents of Mg, Al and Si, predominated in the material obtained by grinding the monolith diesel catalyst (DO, DN) (Table 1). Microphotographs

of the surfaces of the individual catalysts are given in Fig. 1. While the surfaces of the gasoline catalyst (GO, GN) are very similar, DO, in contrast to DN, is covered with needles containing SiO$_2$ and Al$_2$O$_3$ with an approximate stoichiometry of 3:4. Two forms of Al$_2$O$_3$ were identified in the reference material as the predominant phases. The amounts of Pt, Pd and Rh did not significantly differ in GN and GO. The stoichiometries of Pd/Pt (16:1) and Pd/Rh (16:1) given by the manufacturer for GN are similar to the stoichiometries calculated from the measured concentrations (GO Pd/Pt = 16.9, Pd/Rh = 16.4; GN Pd/Pt = 13.5, Pd/Rh = 13.3). The amounts of Pt in the new and used diesel catalysts are very similar (DO 3975 mg kg^{-1}, DN 3851 mg kg^{-1}). In relation to the contents of Pt, Pd and Rh, reference material NIST 2556 is probably a mixture of homogenised monoliths of aluminium oxide, used as gasoline and diesel catalysts.

3.2. Rate of leaching

The rates of leaching of the individual catalysts are apparent from the concentration curves for Pt and Pd depicted in Fig. 2. Three kinetic models were used to express the reaction rates as a function of the effect of diffusion or reaction on the phase boundary [24,31]:

1. The modified Noyes–Whitney equation, yielding the dependence of the rate on the concentration gradient in the vicinity of the dissolved particles. The dependence has the shape:

$$\ln(Ce - C) = \ln Ce - k_1St$$

2. The second parabolic model encompasses both diffusion and the effect of the reaction on the surface of the dissolved particles and is given by the mathematical dependence:

$$\frac{1}{(Ce - C)} = \frac{1}{Ce} + k_2t$$

3. The third model is a combination of dissolution dependent on an unsaturated solution and diffusion in the concentration gradient as a function of the square root of time:

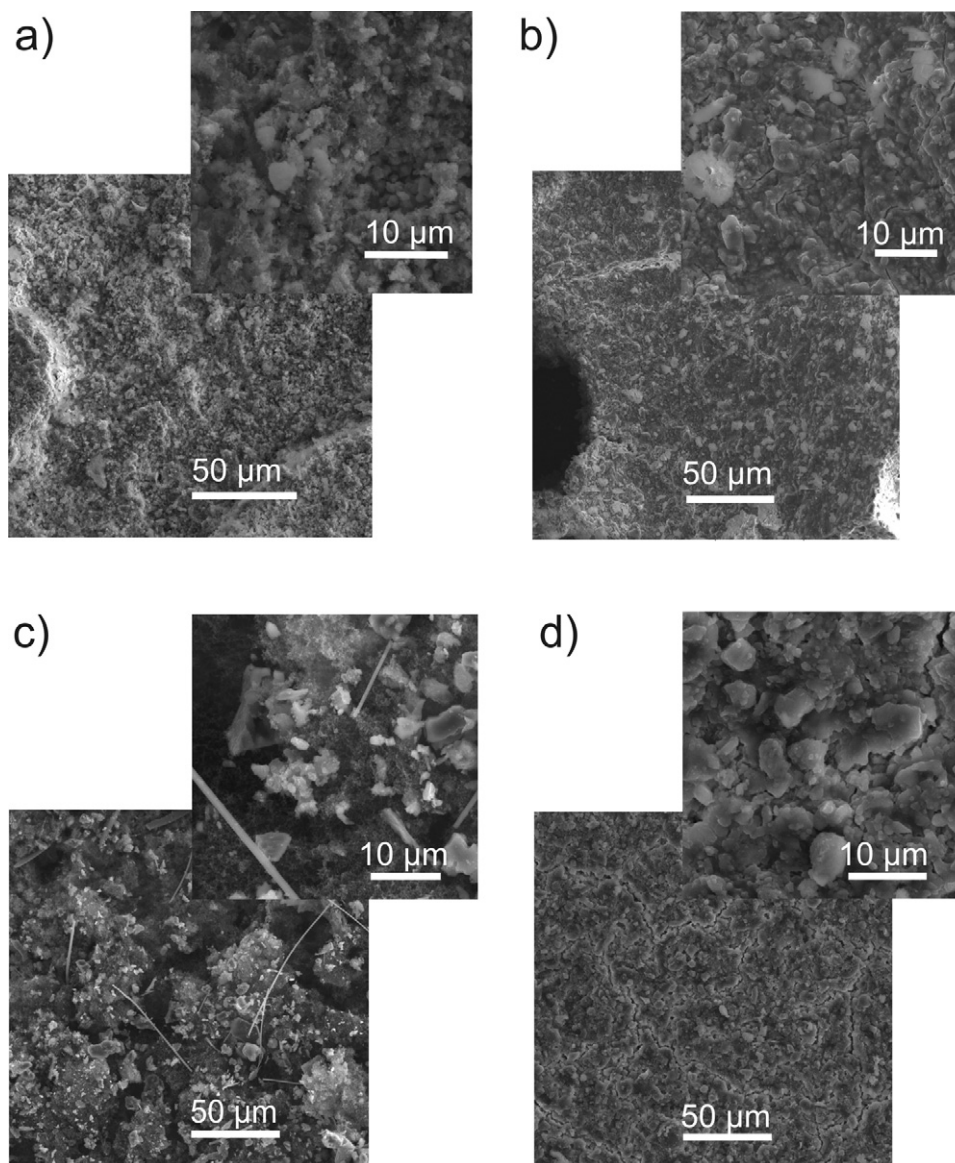$$C = 2 \cdot (Ce - C)\left(\frac{\sqrt{D}}{\pi}\right)t^{1/2} = k_3t^{1/2}$$

Fig. 1. SEM secondary electron image of the catalyst surfaces: (a) surface of catalyst GO, (b) surface of catalyst GN, (c) surface of catalyst DO, (d) surface of catalyst DN. The needle-shaped aggregates of the DO catalyst contain Al and Si oxides in a ratio of approx. 4:3.

In all the models, C is the metal concentration in the solution at time t, Ce is the equilibrium concentration (concentration attained at the longest time or the maximum attained concentration), S is the surface area of the undissolved solid phase, k_1 is a first-order combined rate constant (h^{-1}), k_2 is the rate constant of the second model ($\mu g\,L^{-1}$)$^{-1}\,h^{-1}$, k_3 is the rate constant of the third model ($\mu g\,L^{-1}\,h^{-1/2}$), and D is the diffusion constant. As S and D are assumed to be constants, they do not have any effect on the final calculation and were thus not included in the determination of the rate constants. Fig. 2 depicts the variation in the Pd and Pt concentrations in the individual leachates, the curves corresponding to the individual models and the derived rate constants. The model curves were fitted only in cases where there are no significant fluctuations or decreases in the concentrations of the two metals in time, where metal is released into solution during the actual reaction and where processes of immobilisation do not occur. These cases occur only when using leaching agents CA and NaPyr (Fig. 2). The only exception to this rule is the DO-NaCl interaction, which probably occurs because of the low final pH value. The initial NaCl solution has a pH of 6.36. It is probable that the monolith catalyst from the diesel

motors saturated with NOx emissions releases HNO_3 during leaching; the resultant solutions have a pH ranging from 4.12 to 4.39 after the interaction, and Cl complexes predominate in the speciation.

The leaching is fastest in the CA solution; the kinetic curves for Pd and Pt increase rapidly at the beginning of the experiment, followed by the slow progressive release of both metals into solution. Interactions with CA have a larger rate constant than interactions with NaPyr. The rate constants for the second order kinetic model for Pd vary in the range of 1.2×10^{-6} ($\mu g\,L^{-1}$)$^{-1}\,h^{-1}$ (GN–CA interaction) to 6.8×10^{-3} ($\mu g\,L^{-1}$)$^{-1}\,h^{-1}$ (NIST–CA interaction); the rate constants for Pt vary in the range of 1.8×10^{-8} ($\mu g\,L^{-1}$)$^{-1}\,h^{-1}$ (DN–CA interaction) to 8.6×10^{-4} ($\mu g\,L^{-1}$)$^{-1}\,h^{-1}$ (GO–CA interaction). The rate constants for the GO–CA, GN–CA, GO–NaPyr and GN–NaPyr interactions are larger for Pd than for Pt. It cannot be stated which model is better for the description of these kinetics; in some cases, models 1 and 2 are better (e.g., Pt GO–CA, Pt DO–NaCl), while in others, the shape of the curves is closest to model 3, i.e., processes affected by gradient diffusion (e.g., Pt DN–CA). During the interactions with NaCl and FA, the Pd concentration exhibits an increase and decrease at the beginning of the experiment and then
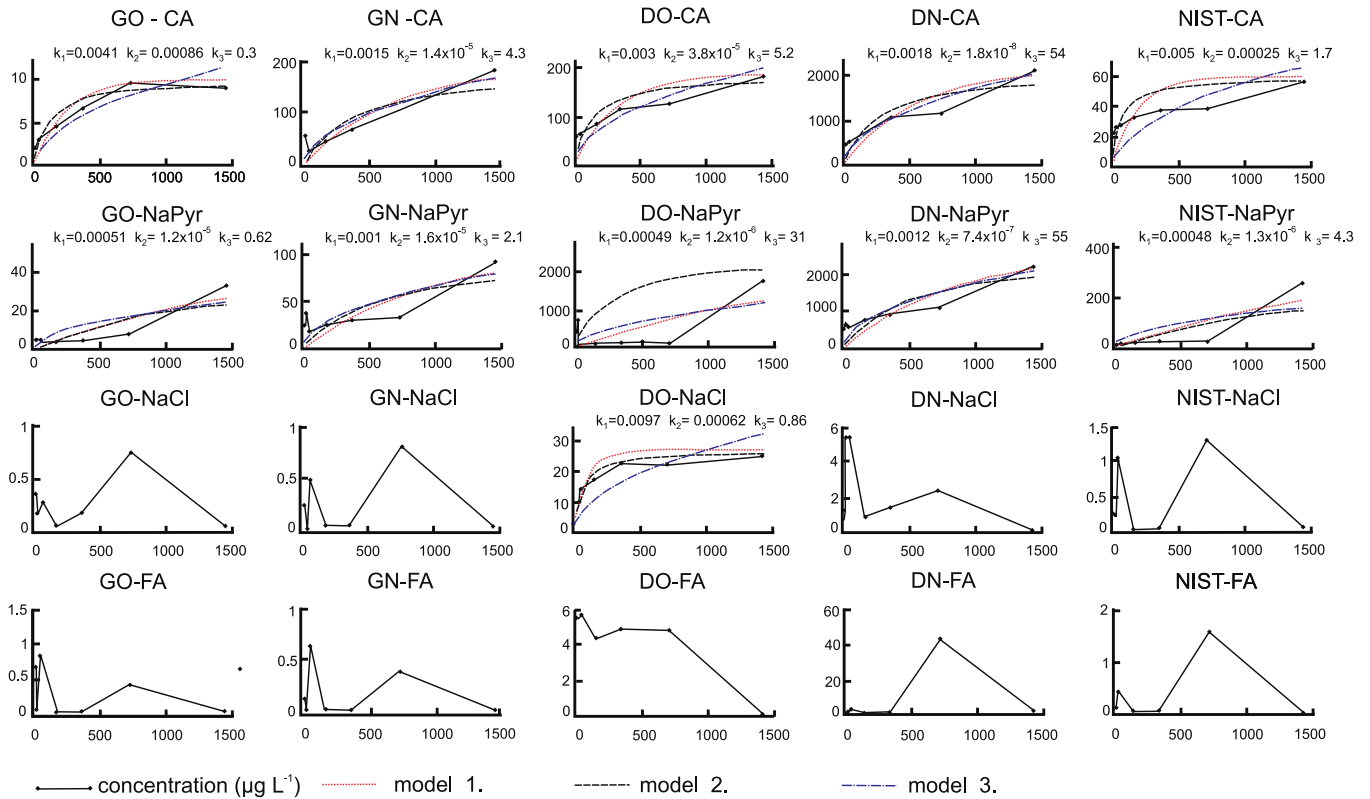
a) Pd
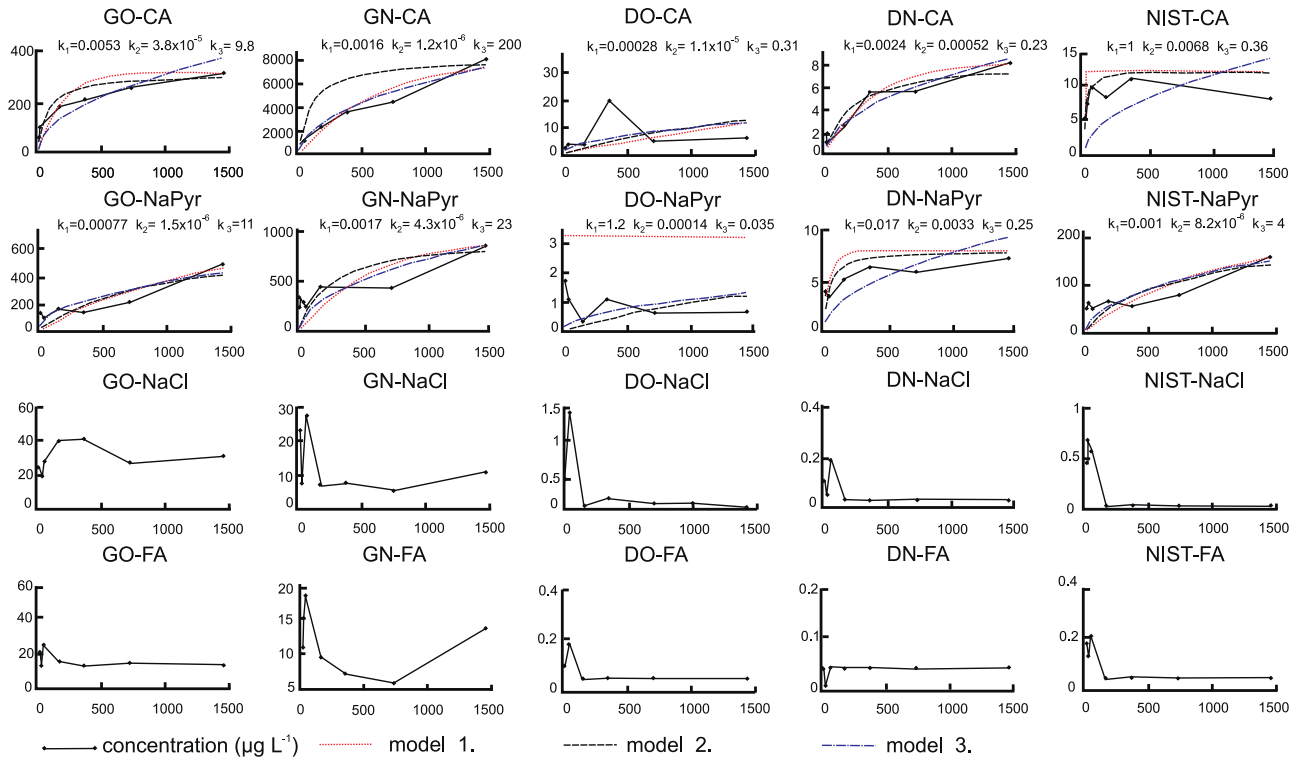
b) Pt

Fig. 2. Trends in the Pd and Pt concentrations released from GO, GN, DO, DN and NIST by leaching with citric acid (CA), sodium pyrophosphate (NaPyr), sodium chloride (NaCl) and fulvic acid solution (FA). Full line – concentration variation (μg L^{-1}), dotted line – kinetic model (1), k_1 (h^{-1}); dashed line – kinetic model (2) k_2 (μg L^{-1})$^{-1}$ h^{-1}; dot-and-dash line–kinetic model (3), k_3 (μg L^{-1} h$^{-1/2}$).
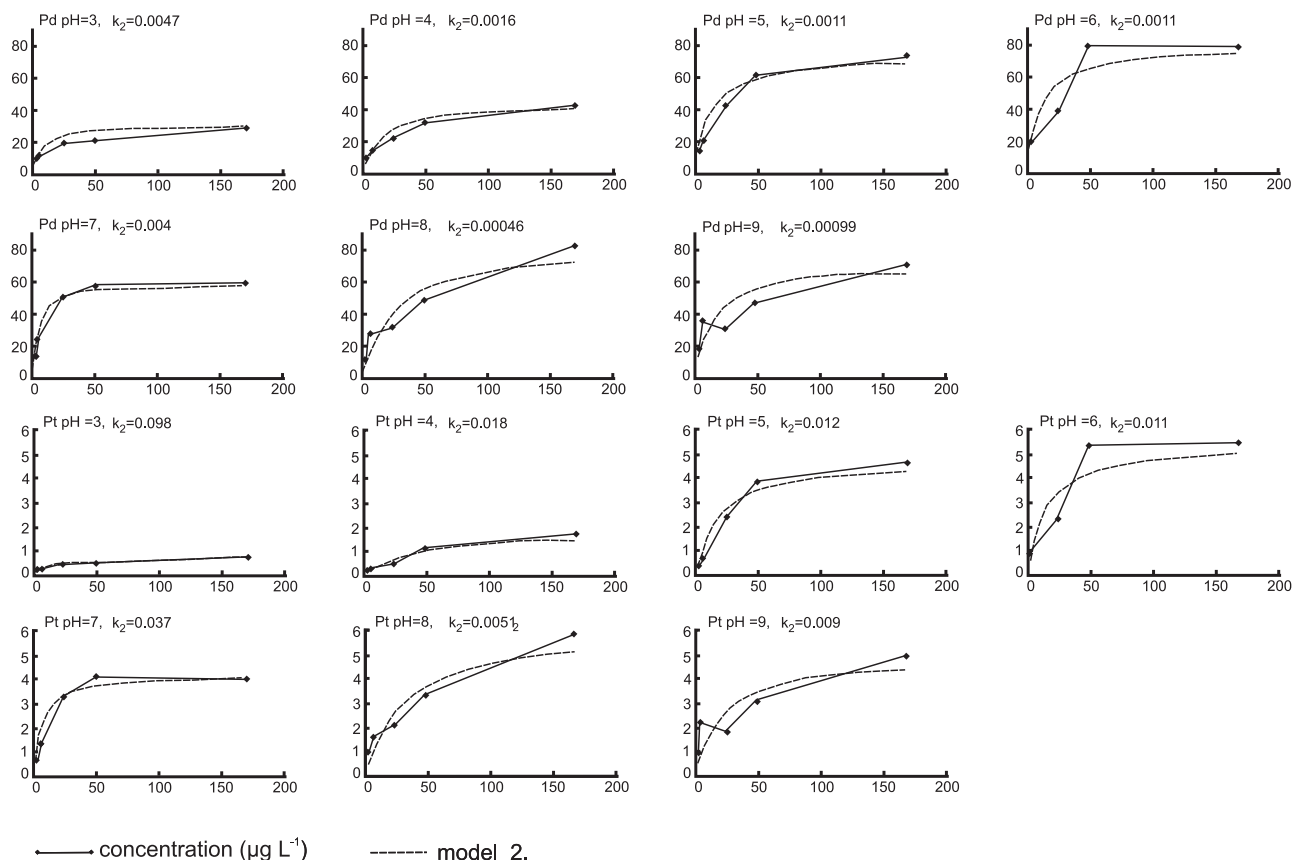
Fig. 3. Variation in the concentrations of Pd and Pt released from GO into 20 mM CA in dependence on the initial pH. The concentration variation ($\mu g\,L^{-1}$) is depicted as the full line. For simplification, only the dependence based on the kinetic model (2) is depicted in the figure, together with the corresponding kinetic constant k_2 ($\mu g\,L^{-1}$)$^{-1}\,h^{-1}$.

a slight increase or no change. During interactions with NaCl or FA, the Pt concentration exhibits an increase, followed by a decrease and then another increase (710 h) and decrease.

The rates for pH static extraction in citric acid are depicted in Fig. 3. During the extraction of GO by CA at pH values of 3, 4, 5, 6, 7, 8 and 9, the final pH equilibrated at values of 3.42, 4.39, 5.64, 7.41, 9.72, 9.93 and 9.94, respectively, after 168 h of interaction. A final pH value > 9 resulting when an initial pH > 7 was used is probably caused by the predominant Al_2O_3 in the particles of the GO catalyst.

The release of Pd and Pt is best represented by model 2. Similarly, Turner and Price [24] designated model 2 (2nd order kinetics) as the most important and closest fit for modelling PGE in acidic media, simulating acidic stomach conditions. For Pd and Pt, the value of k_2, i.e., the extraction rate, decreases faster with increasing pH in the interval of initial pH 3–6 (Fig. 3). The other reaction models and their rate constants do not exhibit this trend.

3.3. Normalised Pt and Pd release

A comparison of the leaching of Pd and Pt from the individual catalysts using the selected leaching agents was performed by calculating the normalised bulk release (NR_i) values used, e.g., in studying alterations in metallurgical waste [32]. The first step consists of a calculation of the bulk release R_i ($\mu g\,m^{-2}$) values defined as the amount of element i released from the unit surface area of the studied substance. The bulk release was calculated from the relationship $R_i = [c_i \times (V/m)]/S$, where c_i is the concentration of element i in the extract ($\mu g\,L^{-1}$), V is the total volume of the leaching agent (L), m is the weight of the sample (g) and S is the specific surface area of the individual catalysts ($m^2\,g^{-1}$). The calculated bulk release R_i was then normalised to the element

concentrations in the leached material according to the equation $NR_i = (R_i \times 10^6)/c_{is}$, where NR_i is the normalised release ($\mu g\,m^{-2}$), R_i is the bulk release ($\mu g\,m^{-2}$) and c_{is} is the concentration of element i in the leached material ($mg\,kg^{-1}$). The values of NR_i are given in Table 2. The highest NR_{Pd} values were exhibited by the interactions DO–CA ($4.6 \times 10^5\,\mu g\,m^{-2}$), DN–CA ($5.9 \times 10^4\,\mu g\,m^{-2}$), DN–NaPyr ($5.2 \times 10^4\,\mu g\,m^{-2}$) and DO–NaPyR ($5.1 \times 10^4\,\mu g\,m^{-2}$). The maximum NR_{Pt} values are one to two orders of magnitude lower than the values calculated for Pd. The highest values are attained in the interactions DO NaPyr ($3.4 \times 10^3\,\mu g\,m^{-2}$), DN NaPyr ($1.38 \times 10^3\,\mu g\,m^{-2}$) and DN CA ($1.3 \times 10^3\,\mu g\,m^{-2}$). In all cases of the interaction with NaCl and FA, with the exception of DO NaCl ($NR_{Pt} = 48.91$), NR_{Pt} and NR_{Pd} are lower at the end of the leaching experiment compared with NR_i max (Pt and Pd). This phenomenon could be related to the effective process of immobilisation of the released Pt metals, which occurs at the catalyst-leaching agent phase boundary.

3.4. Speciation of Pt metals in leachates

It follows from thermodynamic modelling that, in the interaction of the studied catalysts with CA in the pH range between 2.5 and 3, $Pd(OH)_2^0$ (70–92%), $Pd(OH)^+$ (7.9–22%) and Pd^{2+} (0.7–6.8%) predominate in the speciation of Pd. The slightly elevated pH during the leaching leads to an increase in the $Pd(OH)_2^0$ content and decrease in the contents of the $Pd(OH)^+$ and Pd^{2+} forms. The $Pd(OH)_2^0$ form also has a lower content in the leachates from the diesel catalysts and NIST 2556 (this is a mixture of gasoline and diesel catalysts). The forms have a low content of Pd citrates (0.00005 and 0.0001%), from which it follows that these ligands have minimal impact on the solubility and that the main process

Table 2
Comparison of normalised release (NR_i) for various leaching media. The maximum and final NR_i values for the 1440-h leaching procedure are indicated. The strong Pt- and Pd-scavenging mechanisms are indicated in *italics*.

Leaching media	Pt (μg m^{-2})		Pd (μg m^{-2})			Pt (μg m^{-2})		Pd (μg m^{-2})	
	Max	Final	Max	Final		Max	Final	Max	Final
GO					GN				
Citric acid CA	35.79	33.28	70.11	70.11		227	227	754	754
NaPyr	126	126	111	111		120	120	80.60	80.60
NaCl	2.84	*0.22*	9.04	7.00		1.02	*0.08*	2.54	1.04
FA	4.06	*0.22*	9.21	3.00		0.84	*0.08*	1.75	1.30
DO					DN				
Citric acid CA	348	348	467,576	141,515		1301	1301	59,394	59,394
NaPyr	3381	3381	50,909	17,394		1377	1377	51,818	51,818
NaCl	48.91	48.91	32,424	939		3.30	*0.04*	2030	303
FA	11.40	*0.08*	7394	939		26.38	*2.09*	939	303
NIST									
Citric acid CA	120	120	46.54	33.65					
NaPyr	544	544	679	679					
NaCl	2.15	*0.12*	2.83	*0.16*					
FA	3.21	*0.12*	0.85	*0.16*					

of dissolution of Pt metals is determined by the pH. Pt(OH)$^+$ predominates amongst the Pt forms (100%), corresponding to works published previously [30,33]. Variations in the final pH value were observed in leachates prepared using NaCl. While the pH stabilised in the range of 7.8–8.5 in the leaching of gasoline catalysts, the extracts from the diesel catalysts (including SRM) were more acidic, with pH values between 4.16 and 6.39. The Pd forms were dependent on the pH of the solution. The Pd(OH)$_2{}^0$ form corresponded to 100% of the overall speciation of Pd from gasoline catalysts. In contrast to gasoline catalysts, extracts from diesel catalysts have lower pH (4.16–4.29) and much higher contents of the Cl forms (PdCl$_3{}^-$: 66.9–71.2%; PdCl$_2$: 9.8–10.5%; PdCl$_4{}^{2-}$: 9.3–9.9%). Here, the Pd(OH)$_2{}^0$ form has minimal content (7.9–13.5%). The speciation in the other leachates from the diesel catalysts was as follows: Pd(OH)$_2{}^0$ (99.3–100%), PdCl$_3{}^-$ (to 0.6%), PdCl$_2$ and PdCl$_4{}^{2-}$ (only to 0.1% of the total forms). In our case, the effect of the Cl ligands is not as important because of their low concentration (1 g L^{-1} NaCl), as in the case of modelling the interaction with seawater [30]. Amongst the Pt forms, PtOH$^+$ predominates (97.84–99.54% for gasoline catalysts and 99.98–100% for diesel catalysts) with small contents of the Pt(OH)$_2{}^0$ formed (0.46–2.16% for gasoline catalysts and to 0.02% for diesel catalysts).

The extraction performed with CA as a function of pH indicates different speciation of Pd and Pt. In the initial pH interval of 3–6, the predominant form of Pd is the neutral complex Pd(OH)$_2$; only for an initial pH of 7–9 does a small amount of the Pd(OH)$_3{}^-$ complex (<1%) appear in the speciation. For the extraction of Pt at initial pH of 3–6, the Pt(OH)$^+$ complex predominates (>99%); for extraction of Pt at an initial pH of 7–9, the Pt(OH)$_2$ complex appears in the speciation in amounts of 14–44%.

3.5. General implications

The dissolution of Pt and Pd in an exogenic environment is a process that is redox and pH dependent; hydroxyl complexes of these metals predominate in the speciation of Pd and Pt, and the course of the reaction can be described according to the following scheme [30]:

$$Me(s) + nH_2O \rightarrow Me(OH)_n{}^{2-n} + nH^+ + 2e^- \tag{1}$$
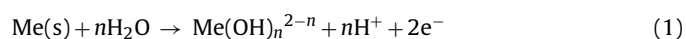
Similar to an electron acceptor, the following reaction can be assumed:

$$1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O \tag{2}$$

When uncharged hydroxyl complexes predominate, the dissolution can be described by the scheme:

$$Me(s) + H_2O + 1/2O_2 \rightarrow Me(OH)_2 \tag{3}$$
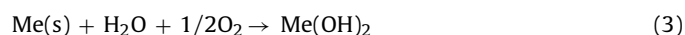
When hydroxyl complexes with a single positive charge predominate, a proton is required for their formation, and the reaction occurs according to the following scheme:

$$Me(s) + 1/2O_2 + H^+ \rightarrow Me(OH)^+ \tag{4}$$
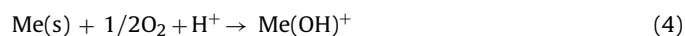
The formation of the most important forms is depicted in the Eh–pH diagram (Fig. 4). Neutral Pd(OH)$_2$ predominates amongst the most numerous Pd forms produced by dissolution of both kinds of catalysts. The process occurs kinetically according to scheme (3) and is dependent on the oxygen diffusion. Positively charged complexes predominate amongst Pt forms (Fig. 4); only in alkaline media NaPyr (pH ∼10, Eh 330 mV) can the predominant Pt form be considered to be neutral Pt(OH)$_2$ [29]. Turner and Price [23] studied the mobilisation of Pt metals from NIST 2556 at low pH (1–4) simulating a gastric solution. The process corresponded best to second-order kinetics (model 2), and the rate constants of this model are 0.015 (μg L^{-1})$^{-1}$ h^{-1} (Pt) and 0.031 (μg L^{-1})$^{-1}$ h^{-1} (Pd). However, the process yields different forms of Pt metals because of the low pH of 2.5 and the high concentration of HCl or other ligands. The rates of leaching of this material (NIST 2556) with a solution of 20 mM CA (pH 2.4–2.8) are approximately an order of magnitude lower in our case (2.5×10^{-4} (μg L^{-1})$^{-1}$ h^{-1} (Pt) and 6.8×10^{-3} (μg L^{-1})$^{-1}$ h^{-1} (Pd)).

The effect of the low pH of the CA solution on the higher rate of this interaction compared to the other leachates is apparent from the high observed rate constants and also the NR_i values. The effect of the pH on the rate of extraction of Pd and Pt from particles of the catalyst GO is apparent from Fig. 3. With an increase in the initial pH (3, 4, 5 and 6), k_2 (Pd) decreases in the order 0.0047, 0.0016, 0.0011 and 0.0011 (μg L^{-1})$^{-1}$ h^{-1}, respectively, and k_2 (Pt) decreases in the order 0.098, 0.018, 0.012 and 0.011 (μg L^{-1})$^{-1}$ h^{-1}, respectively. A neutral complex of Pd is formed and is not adsorbed.

Similar interactions with NaPyr produce neutral Pt complexes that remain in solution and are not removed by processes that can occur subsequently at the phase boundaries. The positively charged Pt(OH)$^+$ complex is also unable to bond in acidic medium (where positively charged mineral surfaces predominate) and remains in solution. The interaction with NaCl does not produce chloride complexes and, because of the higher pH, reaction (4) occurs more slowly, and the charged hydroxyl complexes can be readsorbed on
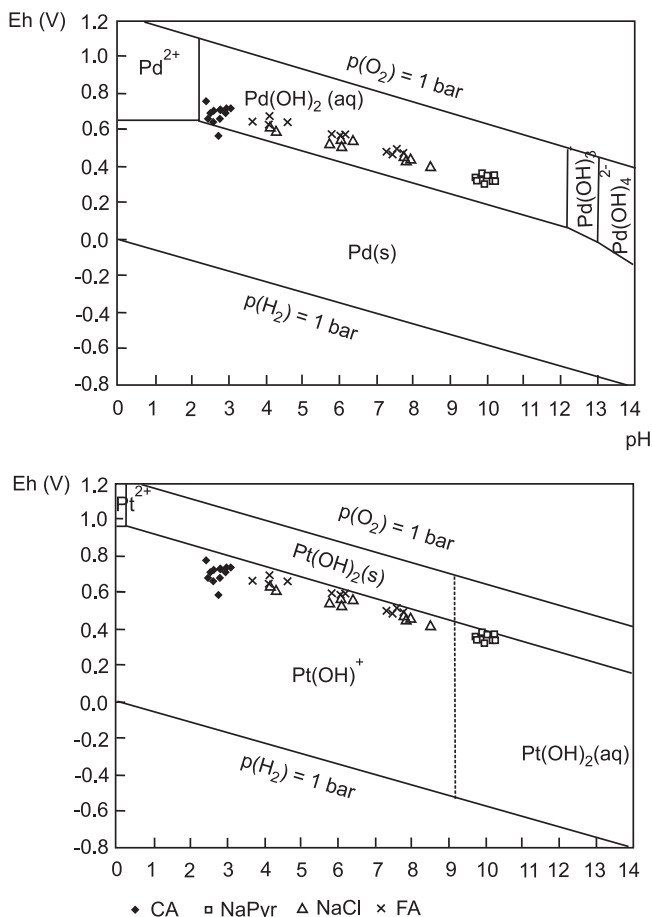
Fig. 4. (a) Eh–pH diagram for Pd for an overall Pd concentration of 10^{-9} M. This was modified according to Colombo et al. [33]; (b) Eh–pH diagram for the total Pt activity at a Pt concentration of 10^{-10} M. This was modified according to Azaroual et al. [30]. The individual points depicted in the diagrams correspond to the blank (Eh, pH parameters of the leaching agent used) and the Eh and pH parameters of the interactions after 1 and 1440 h.

Fig. 5. Energy dispersive spectra of powder particles of pure catalyst GN (a) and powder particles GN after 1440 h of interaction with FA; (b) A substantially higher peak of C taken from the surface of the studied particles is apparent in the spectra of sample (b). The Au peak was derived from the gold-plated sample.

the surface of the leached solid phases, which then have a protonised surface. The lower initial pH of the catalysts affected by emissions and the higher content of Cl forms led to a more rapid release of Pd during the DO–NaCl interaction. Leaching with FA is also characterised by lower NR_i values. Humic substances play a substantial role in the transport and fixation of PGEs [11]. However, HMW organic acids can also act as reducing agents during the oxidation process, can modify the surface of the solid phases on which mobilised PGEs are subsequently adsorbed, or can affect the movement of reactants and reaction products towards the reacting particles. Lustig et al. [13] observed the formation of insoluble Pt-humic complexes during the leaching of tunnel dust and Pt black. Wood [10] described major differences in the Pt contents in experimental solutions containing FA and varying pore sizes of the membrane filter and explained these findings based on the sizes of these complexes. The bonding of PGEs on the surface of the solid phases with humic substances may occur via flocculation of FA bonding Pt metals. These processes can occur even in the case of interactions of these catalysts with the FA employed. Fig. 5 depicts the energy dispersive spectra for experiments with the GN and GN after 1440 h of interaction with FA. Following its interaction with FA, the catalyst exhibits a far greater carbon content on the surface of the individual particles than the catalyst originally used in the experiment, and it can be assumed that this is caused by a coating of the leachate employed (FA) on the catalyst surface.
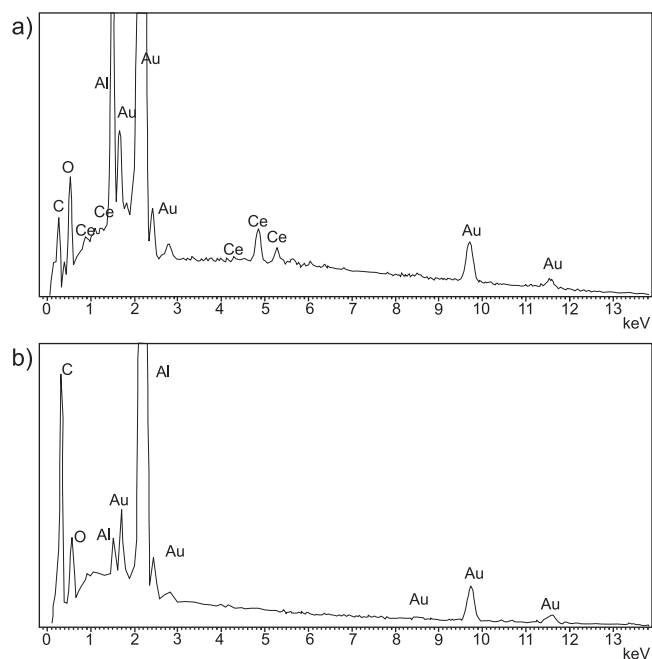
4. Conclusion

It follows from comparison of the mobilisation of Pd and Pt from automobile catalysts by simple complexing agents contained in the soil that this dissolution is dependent mainly on the pH. Simple second-order kinetic models can be used for the interaction with CA, and the reactions seem to be dependent mostly on the pH. Dissolution in acid solutions of CA and alkaline solutions of NaPyr occurs most rapidly. In interactions with other extractants over a longer time scale, processes of back capture of the released metal on the catalyst particles come into effect, preventing assignment of a simple kinetic model.

The employed agents and their ligands have a minimum effect on the speciation of the final products. Neutral or positively charged hydroxyl complexes of Pd and Pt predominate in the modelled speciation of both final forms. If uncharged complexes are formed in the dissolution, they are mobile and remain in solution; charged complexes can be adsorbed on the surface of the remaining solid phases. Sodium chloride in the concentrations employed, which could be derived from melt waters formed during winter road treatment, does not have a substantial impact on the speciation and mobilisation of Pt metals. Similarly, HMW FA covers the surface of the individual particles, and only a very small amount of Pd and Pt are dissolved during its interactions with the solution.

Similar processes can occur in the soil environment in the vicinity of roadways where Pt metals emitted from automobile catalysts could be present. Hydroxyl forms of Pt metals can be formed during interactions with solutions present in soils. However, the mobility of the positively charged complexes can also be affected by adsorption-desorption mechanisms involving other sorbents present in the soils, especially oxides, hydroxides and clay minerals.

Because of the increasing amount of PGEs emitted into the environment, it is necessary in future research to concentrate on: a detailed study of their mobilisation from catalyzer components in dependence on the redox conditions and ionic strength of the individual ligands. Simultaneously it is necessary to direct future studies of the behaviour of PGEs towards their speciation as

colloidal, complex particles or ionic forms. This information will enable assessment of subsequent movement of PGEs in the natural environment.

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