Combined Microwave Assisted Roasting and Leaching to Recover Platinum Group Metals from Spent Automotive Catalysts

Jeroen Spooren[a,*] and Thomas Abo Atia[a]

[a] Waste Recycling Technologies, Sustainable Materials Management, Flemish Institute for Technological Research, VITO N.V., Boeretang 200, 2400 Mol, Belgium.

* Corresponding author. E-mail: jeroen.spooren@vito.be; phone: +32 14 33 56 33

A microwave assisted two-step platinum group metal (PGM) extraction process for spent automotive ceramic catalysts was developed. The first step consists of a microwave (MW) sulfation roasting process of spent catalyst in the presence of $NaHSO_4 \cdot H_2O$ or $KHSO_4$ and $NaClO_3$, for which the roasting parameters (*i.e.* MW power, roasting time, ClO_3^-:HSO_4^- molar ratio, salt:catalyst weight ratio) were studied and optimized. During roasting a solid salt mixture and spent catalyst (weight ratio salt:spent catalyst = 5, molar ratio $NaClO_3$:$NaHSO_4 \cdot H_2O$ = 0.05) was volumetric heated (750 W, 30 min) through absorption of MWs without the use of any other heat source. Whereas for the subsequent step, a short (30 min, 105 °C) MW acidic leaching process in 1 M HCl solution at a liquid to salt ratio of 10 was evaluated to give the best PGM leachabilities (*i.e.* Pd 96 ±1%, Pt 85 ±5% and Rh >96%). An in depth experimental study of the roasting process showed that sulfation roasting attacks both the cordierite ($Mg_2Al_4Si_5O_{18}$) honeycomb material and rare earth oxides of the wash coat, to form sulfate salts. During roasting metallic Pd oxidized. Mass loss during roasting was ascribed to evaporation of $NaHSO_4 \cdot H_2O$ hydration water and subsequent decomposition of $NaHSO_4$.

Keywords: PGM recovery, sulfation roasting, microwave roasting, microwave leaching, recycling, spent automotive catalyst

1 Introduction

Conventionally, the recycling of spent automotive catalysts, whereby platinum group metals (PGMs) are recovered, is carried out by pyrometallurgical processes. Such processes have intensive energy consumption since they operate between 1450 and 1900 °C [1, 2].
Nowadays, research efforts focus on developing hydrometallurgical methods whereby PGMs are leached from the catalysts materials using acidic or alkaline solutions in the presence of oxidizing agents, such as chlorine, nitric acid, hydrogen peroxide, sodium cyanide solutions [3]. The principal disadvantages of hydrometallurgical operation are the longer process times (>4 h) required to achieve high metal recovery, as well as low PGM leaching, in particular for Rh (<85%). These problems are due to the chemical inertness of precious metals, which hardly dissolve in ordinary acids. Therefore, a large amount of strong acid with additional strong oxidant is required for an optimal dissolution. Furthermore, an equally large amount of waste water containing heavy metals and strong acid is generated [4]. Therefore, more effective dissolution processes for the recovery of PGMs should be developed. For instance, recently, novel leaching routes have been described that attempt to tackle these problems with limited success: (i) Oxidative leaching with cupric ions in HCl media achieved 95% Pd and 86% Rh leaching under optimized conditions (T = 80 °C, t = 4 h, [HCl] = 6 M, [Cu^{2+}] = 0.3 M) [5]. (ii) (ii) Electro-generated chlorine was used as an oxidant in HCl solution, which is efficient and eco-friendly for simultaneous PGMs leaching while recycling the unconsumed chlorine gas by reduction on the cathode to neutralize the toxic gas [6]. However, the leaching efficiency of Rh was 65% at 80 °C, 8 M HCl, 4 h.

Microwave assisted leaching has been investigated in an attempt to improve the yield of extracted metal and to reduce process time, especially with the increasing demand for more environmental friendly processes. Unique microwave (MW) heating characteristics are the main driver for potential implementation in metal extraction. These include: low processing time, direct, selective heating, and a more controllable heating process [7, 8].
Chen *et al.* and Wang *et al.* reported that microwave assisted sulfation roasting at a MW power of 300 - 330 W with $NaHSO_4$ as a sulfate source and in the presence of an oxidant, $NaClO_3$, for extracting Pd and Rh from spent automobile catalysts could enhance leaching efficiency up to 99% Pd and 95% Rh as well as decrease reaction times (30 min for Pd, 60 min for Rh) [9, 10]. With respect to sulfation roasting by conventional heating, MW assisted roasting lead

to a shorter roasting and leaching times and improved leaching efficiency. However, the authors did not investigate the extraction of Pt. Batista et al. described the sulfation roasting of a commercial Pt-based catalyst with KHSO4 as a sulfate source, but in the absence of an oxidizing agent [11]. In this case, Pt did not react and consequently did not dissolve during the subsequent water leaching step.

Suoranta *et al.* showed microwave assisted leaching of Pd, Pt, Rh and Ru in aqua regia and HCl to leach >90% of Pd, Pt, Rh and Ru at temperatures above 150 °C [12]. They also investigated PGM leaching at high pressures instead of by microwave heating. The results showed that microwave assisted leaching (Pd 87±2%, Pt 78±3%, Rh 79±3%) was more efficient than leaching using conventional heating (Pd 35±13%, Pt 6±2%, Rh 20±1%). Furthermore, the difference in the recoveries of PGMs also indicated that phenomenon occurring in microwave heating, such as local superheating of the leach solution or selective heating of the catalyst material, can have a favorable effect on dissolution of PGMs.

This work aims to apply a fully MW-assisted two step PGM extraction process of spent automotive catalysts. The first step consists of a MW sulfation roasting process for which the roasting parameters were studied and optimized. Whereas, for the second step a short MW acidic leaching process was developed.

2 Materials and methods

2.1 Materials

A representative sample of spent automotive catalysts was provided by MONOLITHOS Catalysts Ltd. (Greece). The sample was produced by collecting 100 spent ceramic catalytic converters which have been de-canned to yield 87.7 kg of spent automotive honeycomb. This material was subsequently milled to <2 mm and a representative sample (5 kg) of this milled material has been further ball-milled to <0.16 mm. The latter material (<0.16 mm) was fully characterized and used in this study.

Reagents used for roasting experiments were $NaHSO_4 \cdot H_2O$ (Merck, extra pure, ≥99.0%) or $KHSO_4$ (Merck, p.a., ≥99.0%) as sulfate sources and $NaClO_3$ (Alfa Aesar, granular, ≥99%), NaOCl (Merck, 6-14%) or H_2O_2 (Fisher Scientific, 12%) as oxidation agents. During leaching, de-ionized water (Milli-Q) was used or a solution of HCl (Merck, fuming 37% p.a.).

2.2 Experimental

Microwave assisted roasting experiments were performed in a Milestone PyroWave microwave furnace, equipped with a 1.2 kW magnetron and operating at a MW frequency of 2450 MHz. The maximum operating temperature of this system is 1200 °C. A small amount of milled catalyst material (0.5 - 1 g) was mixed with the desired amount of sulfate salt and oxidation agent by means of pestle and mortar. Consequently, the mixture was transferred in a ceramic crucible that was place in the microwave furnace. In the microwave furnace the heating of samples occurs through volumetric heating by absorption of MW radiation by the sample materials. The reaction is steered by applying a chosen microwave power of 750 W for a chosen time period. In this set-up, no temperature control during reaction takes place and the temperature of the samples is measured at the end of the microwave program by means of an infrared thermometer (VOLTCRAFT IR-2200-50D).

Conventional water leaching after roasting took place by transferring the roasted material in a beaker, which was filled by a known amount of de-ionized water at 60 °C. The beaker was placed for 30 min in a water bath at 60 °C under constant shaking. After reaction, the slurry was cooled to room temperature and the pH and conductivity were measured. Next, the slurry was filtered (Whatman ME 0.45 µm membrane filter) and the leachate was conserved for further analyses and the solid residue dried at 105 °C.

Microwave assisted leaching was performed in a Milestone FlexiWave oven, equipped with a dual magnetron system (950 W each) and operating at a MW frequency of 2450 MHz. The MW cavity is equipped with a carousel system that contains 15 closed Teflon® reactor vessels with a volume of 100 mL each. The maximum operating temperature is 300 °C and pressure 100 bar. The roasted samples are brought in the reaction vessel with 40 mL of lixiviant (de-ionized (DI) water or 0.1 M or 1 M HCl solution) after which the oven is heated to a chosen temperature in 10 min and kept at the chosen temperature for 15 min. After cooling of the reaction mixture, the same procedure as described above (conventional water leaching) was followed.

2.3 Analyses

The chemical composition of solids, including the starting material and residues after leaching, were analyzed by means of ICP-AES (THERMO OPTEK IRIS

ADVANTAGE), after microwave digestion. The total carbon concentration was measured by a Multi EA4000 apparatus of Analytic Jena. Whereas, their mineralogy was measured by XRD (PANalytical EMPYREAN) with Co Kα radiation. The concentration of dissolved elements in the eluates was measured by ICP-AES. Thermogravimetric analysis (TGA) was carried out using a STA 449 F3 Jupiter (Netzsch, Germany) in dry air (50 ml/min). The salts $NaHSO_4 \cdot H_2O$, $NaClO_3$ and a mixture thereof as well as a mixture of both salts with the spent catalyst were analyzed from room temperature to 1000 °C (10 °C/min). The TGA device was coupled online with a quadrupole mass spectrometer TGA/STA-QMS 403 D Aëolos (Netzsch, Germany) with a heated capillary (200 °C). Statistical design of experiment calculations was performed by the software Statistica 12.0.

X-ray photoelectron spectroscopy (XPS) measurements were performed by using a Physical Electronics (PHI) 5800-01 spectrometer. A monochromatic Al Kα X-ray source was used at a power of 350 W. The pressure in the analysis chamber of the spectrometer was 1×10^{-9} Torr during the measurements. The Ag $3d_{5/2}$ peak of an Ag foil was taken, after argon sputtering, for checking the calibration of the binding energy (BE) scale. XPS data have been interpreted by using the online library of oxidation states implemented in the PHI MULTIPAK 6.1 software and the PHI Handbook of X-ray Photoelectron Spectroscopy [13].

3 Results and discussion

3.1 Characteristics of spent ceramic automotive catalyst sample

The elemental composition of the spent automotive catalyst powder is given in Table 1. The PGMs present in the starting material were Pd (1670 mg/kg), Pt (958 mg/kg) and Rh (318 mg/kg). The honeycomb material of the catalyst is cordierite and the wash coat is composed of a mixture of ZrO_2 and CeO_2. These three mineral phases were observed by XRD. Also, a SiO_2 zeolite-like phase was detectable, whereas the presence of a PdO phase was somewhat speculative (*i.e.* assignment based on one small peak).

Table 1: Elemental composition of a representative sample of milled (<0.16 mm) spent automotive catalysts, measured by ICP-AES and total carbon measurement.

Element	**Composition (mg/kg ds)**
Mg	52300
Al	168000
Si	110000
Ca	3300
Ti	3170
Fe	7130
Zn	2810
Zr	27300
Rh	318
Pd	1670
Pt	958
Ce	22300
La	2320
Total Sulphur	2240
Total Phosphor	5130
Total Carbon	1800

3.2 Parameter optimization of MW sulfation roasting followed by water leaching

First, the PGM leaching from the studied spent automotive catalyst material by means of MW assisted sulfation roasting followed by water leaching was optimized. Different sulfate sources and oxidation agents were screened as possible reagents for MW sulfation roasting of spent automotive catalyst material. To 1 g of spent catalyst material a sulfate source (7.5 g $NaHSO_4 \cdot H_2O$, 8.37 g $KHSO_4$ or 0.5 g H_2SO_4 solution) and in some cases an oxidation agent (2.5 g $NaClO_3$, 5 mL NaOCl or 5 mL H_2O_2) were added. After mixing by pestle and mortar the materials were MW roasted at 750 W for 30 min. Subsequently the roasted materials were leached in 100 mL of DI water for 30 min at 60 °C. The PGM leaching of $KHSO_4$ roasted autocatalyst was most effective for PGM recovery, especially in the case of Pt (Figure 1). However, it needs to be noted that Rh and Pd leaching of NaHSO4·H2O treated materials gives very similar results

and from an economic perspective $NaHSO_4 \cdot H_2O$ is cheaper than $KHSO_4$. $NaClO_3$ is the preferred oxidation agent.

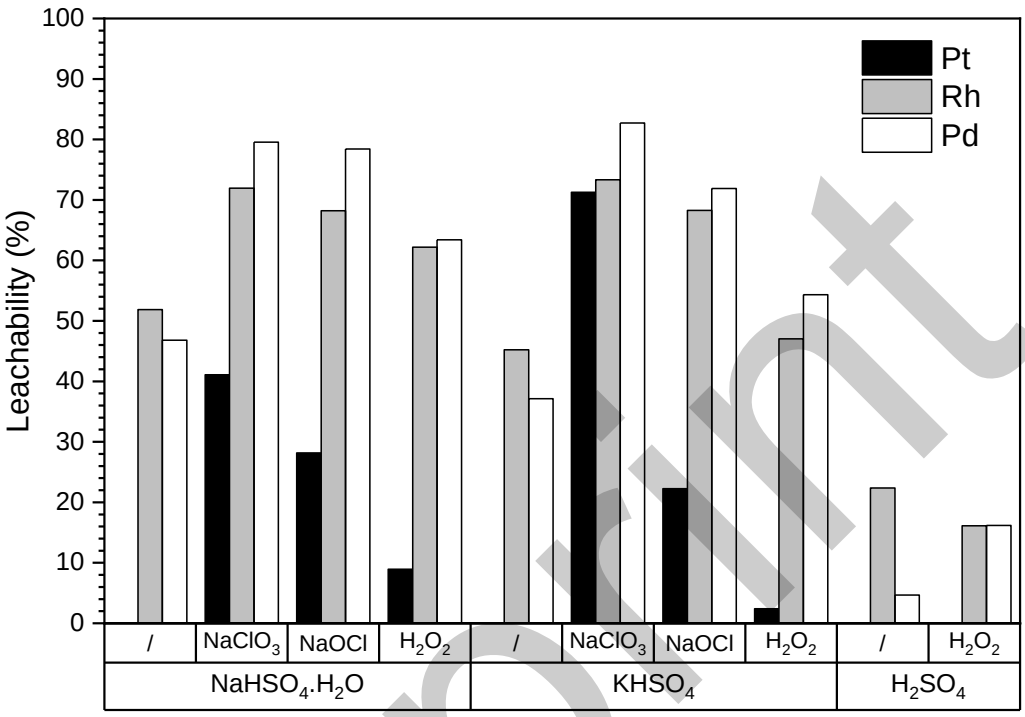

Figure 1: PGM leachabilities in water at 60 °C for 30 min, after a roasting step at 750 W for 30 min of spent automotive catalyst with different sulfate sources and oxidation agents in a 1:10 ratio. Oxidizing agents were added in a 1:3 weight ratio in respect to the amount of sulfate salt.

The influence of the molar ratio of oxidation agent ($NaClO_3$) versus bisulfate (HSO_4^-) (0.1, 0.2, 0.3, 0.4 and 0.5) on PGM leachability after MW roasting was tested for both $KHSO_4$ and $NaHSO_4 \cdot H_2O$ as sulfate source. No clear trend of PGM leachability as a function of the amount of chlorate addition was observed (Figure 2). However, in the total absence of $NaClO_3$, the water leaching of Pt is reduced to 0% and that of Rh and Pd is lower with respect to material which was roasted in the presence of $NaClO_3$. Additional, it needs to be observed that the measured Pt leachability has a very large error margin. Pt seems to be more stable than Pd and Rh towards sulfation roasting followed by water leaching.

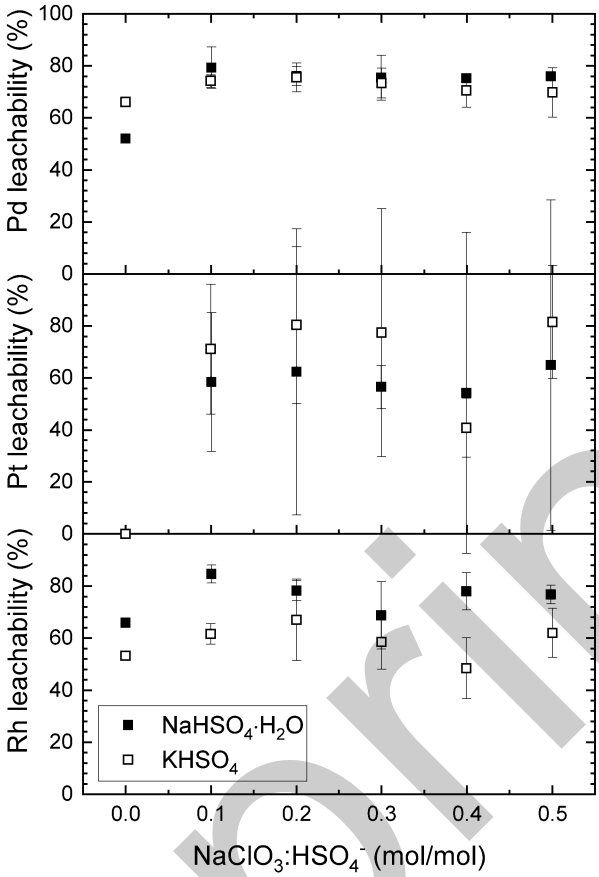

Figure 2: Leachability of Pd, Pt and Rh in water at 60 °C for 30 min, after a roasting step at 750 W for 30 min of spent automotive catalyst with different sulfate sources ($NaHSO_4 \cdot H_2O$ and $KHSO_4$). The oxidizing agents $NaClO_3$ was added in different molar ratios in respect to the amount of sulfate salt.

In a following experiment the salt mixture to catalyst ratio was evaluated, since a lower consumption of salts benefits the economics and material consumption of the process. Furthermore, the liquid to salt ratio (L/S) of the water leaching step is determined by the amount of salt used and consequently when less salt is used for roasting, less leachate per amount of catalyst is created with a higher concentration of leached metals, such as PGMs. The spent catalyst was MW roasted in the presence of two different $NaHSO_4 \cdot H_2O$:$NaClO_3$ salt mixtures, whereby the molar ratio HSO_4^-:ClO_3^- was varied between 0.24 and 0.58. Five weight ratios salt:spent catalyst were tested (1, 2.5, 5, 7.5 and 10) and the water leaching took place at a liquid to salt ratio of 10. Figure 3 shows that the leachability of Pd and Rh does not change significantly at salt to spent catalyst weight ratios of 5, 7.5 and 10. Whereas, at weight ratios of 1 and 2.5 their water leachabilities drop.

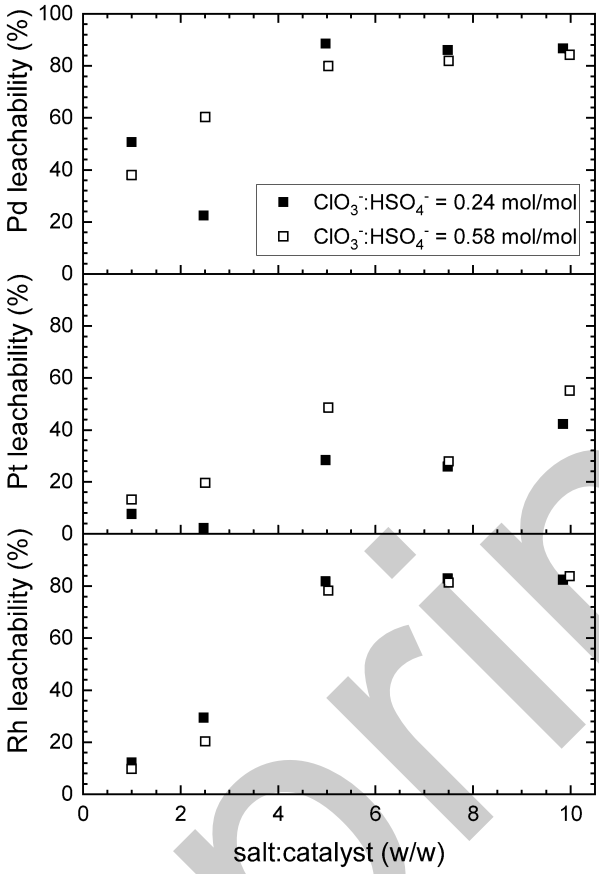

Figure 3: Leachability of Pd, Pt and Rh at two molar ratios of ClO_3^-:HSO_4^- as a function of salt:autocatalyst mass ratio. MW roasting took place at 750 W for 30 min, subsequent water leaching at 60 °C for 30 min.

3.3 Parameter optimization for MW sulfation roasting followed by MW leaching

It is known that PGM leaching requires harsh leaching conditions [4]. In the case of the above experiments (Figure 2 and Figure 3), the pH of the leachate ranged between 1.30 and 3.80 and the oxidation reduction potential (ORP) between 450 and 1130 mV (vs Ag/AgCl electrode). In order to increase the leachability of PGM after MW sulfation roasting, the subsequent leaching step needed further improvement. On the one hand, water leaching was tested at higher temperatures and heating was applied by MW irradiation in order to have a fast heating rate. On the other hand, addition of HCl to the leaching liquor was tested as a mean to decrease pH and supply chloride anions, which are known to easily form soluble complexes with PGMs [12].

Samples were roasted at 750 W for 30 min whereby the salt:spent catalyst mass ratio was 10:1 and the $NaClO_3$:$NaHSO_4 \cdot H_2O$ molar ratio was 0.43. Subsequently the

samples were leached at varying conditions at a liquid to original amount of salt ratio of 10. Roasted samples were first leached in DI water at 60 °C by conventional heating and by MW heating at 60, 105 and 150 °C. A marked difference in Pt leachability at 60 °C is observed when the reaction is heated conventionally or by MWs (Figure 4). Furthermore, the Pt leachability in DI water increases upon increasing temperature when MW leached, whereas the Pd and Rh leachability do not vary significantly as a function of MW leaching temperature. When the lixiviant was a 0.1 M HCl solution, the MW leachability of all PGMs improved with respect to MW leaching with DI water. The leachability of PGMs in 0.1 M HCl was highest (Pd 89%, Pt 82%, Rh 85%) at a leaching temperature of 105 °C (Figure 4).

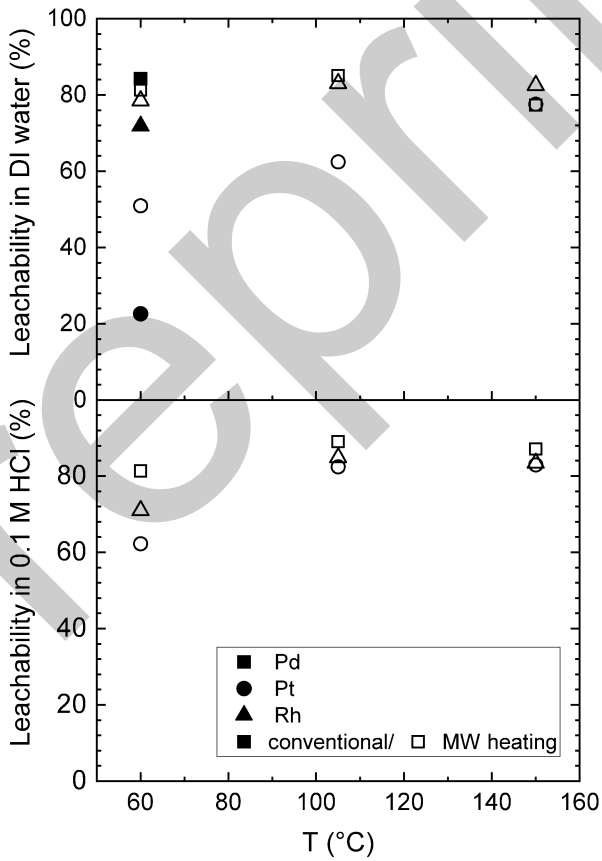

Figure 4: PGM leachability in DI water and in a 0.1 M HCl solution of MW sulfation roasted spent automotive catalyst as a function of the leaching temperature. Full symbols refer to conventional heated, while open symbols to MW heated leaching experiments.

To further optimize the process of MW sulfation roasting followed by MW HCl leaching, a design of experiment (DoE) (4 factors, 2 replicates) was constructed

wherein two roasting parameters (weight ratio salt:spent catalyst (5, 2.5), molar ratio $NaClO_3$:$NaHSO_4 \cdot H_2O$ (0.2, 0.05)) and two leaching parameters (HCl concentration (1, 0.1 M), liquid to salt ratio (5, 10)) were varied in a full factorial experiment. The MW roasting was performed at 750 W for 30 min, while the MW leaching took place at 105 °C for 30 min. For each experiment the Pd, Pt and Rh leachabilities were analyzed (see Supplementary Information).

During DoE calculation, the tested parameters were represented by a letter: A (weight ratio salt:catalyst), B (molar ratio ClO_3^-:HSO_4^-), C (liquid to salt ratio) and D (HCl concentration). The standardized effects, measured within the DoE, of the tested parameters on the leachability of the PGMs (Pd, Pt and Rh) showed that the salt to catalyst weight ratio during roasting is significant (*i.e.* p <0.05) and has a positive effect, meaning that a high salt to catalyst weight ratio of 5 improves PGM leachability. In the case of Pt and, to a lesser extent, Rh leaching, the amount of added $NaClO_3$ oxidizing agent during roasting has a significant negative effect, thus a low ClO_3^-:HSO_4^- molar ratio of 0.05 gives better Pt and Rh leaching. However, it needs to be noted that the presence of the oxidation agent remains necessary (Figure 2). For Pt, the reduced leachability in a relatively weak acid at high oxidation potential can be related to the formation of a Pt-oxide passivation layer on the PGM surface, as described by Hodnik *et al.* [14]. The L/S ratio during MW leaching is significant for Pt and Rh, but the effect is both positive and negative, respectively. Finally the HCl concentration has a strong significant positive effect on the Pt leachability.

A plot of the desirability of the investigated parameters (Figure 5), based on the measured Pd, Pt and Rh leachabilities, show that the parameters A, C and D need to be high and B low to obtain optimal PGM leachability. Therefore, the ideal parameters in this study were weight ratio salt:spent catalyst = 5, molar ratio $NaClO_3$:$NaHSO_4 \cdot H_2O$ = 0.05, L/S = 10 and [HCl] = 1 M, which yielded leachabilities for Pd, Pt and Rh of 86 ±2%, 69 ±5% and 89 ±1%, respectively. These leachabilities were calculated based on the concentration of PGMs in the leachate. However, the total concentration of Pd, Pt and Rh in the recovered solid residue (0.34 g) were measured to be 97 ±18 mg/kg, 207 ±66 mg/kg and <20 mg/kg, respectively, leading to leachabilities of 96 ±1%, 85 ±5% and >96%, respectively.

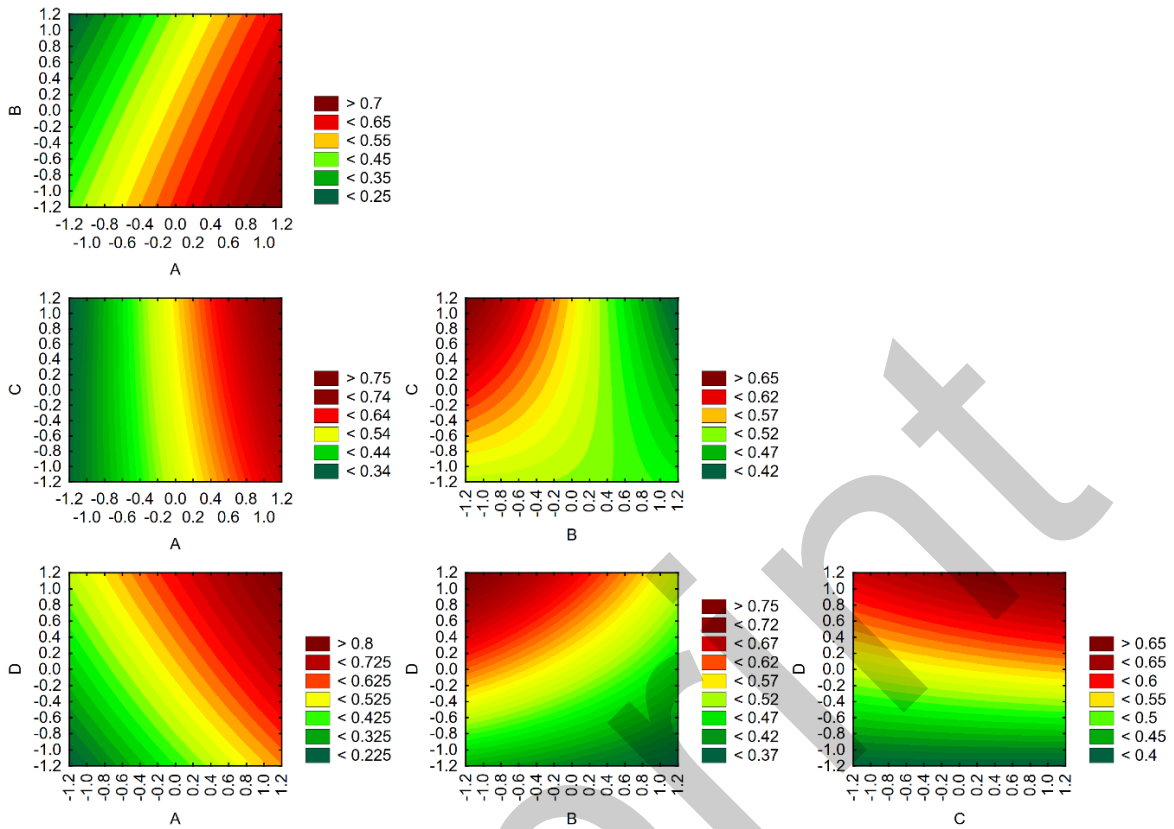

Figure 5: Desirability contour plots of the effect (A, B, C, D) interactions for optimal PGM (Pd, Pt, Rh) leachability. Graphs were obtained by the software Statistica 12.0.

3.4 Study of the MW sulfation roasting reaction mechanisms

The effect of oxidative sulfation roasting on spent car catalysts was studied in more detail. XRD analyses of roasted sample (ratio salt:spent catalyst = 5, molar ratio $NaClO_3$:$NaHSO_4 \cdot H_2O$ = 0.05, 750 W, 30 min) is given in Figure 6. No mineral phases of the originally added salts $NaClO_3$ and $NaHSO_4 \cdot H_2O$ were observed, as they are consumed during the roasting process. Particularly, $NaHSO_4 \cdot H_2O$ reacted with the cordierite ($Mg_2Al_4Si_5O_{18}$) honeycomb material and La, which is present in the wash coat, to form $Na_3Al(SO_4)_3$ and $Na_{1.788}La_{0.062}SO_4$, respectively. Not all cordierite reacted during roasting or dissolved during the subsequent MW leaching in 1 M HCl step (liquid to salt ratio = 10, 105 °C, 30 min). During leaching the sodium sulfate salts were dissolved and the remaining material contains mineral cordierite, and small amounts of mullite, which is likely produced from cordierite during roasting and leaching, and $NaCe(SO_4)_2 \cdot H_2O$, which was precipitated during leaching (Figure 6). Um and Hirato described a $NaCe(SO_4)_2 \cdot H_2O$ synthesis process in sulfuric acid, whereby

the precipitation reaction kinetics of $NaCe(SO_4)_2 \cdot H_2O$ from dissolved Ce^{4+} and Na_2SO_4 was very fast. [15].

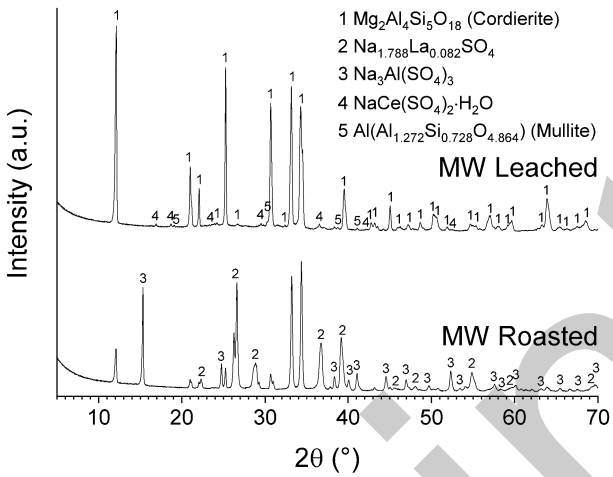

Figure 6: X-ray powder diffractograms of MW roasted spent automotive catalyst sample in the presence of $NaHSO_4 \cdot H_2O$ and $NaClO_3$ and MW roasted sample after MW leaching (1 M HCl).

As shown by XRD analyses (Figure 6), the salts react during MW roasting. Thermogravimetric analyses (TGA), coupled to a mass spectrometer (MS) was used to measure the composition of the released gasses at certain temperatures for the salts used during roasting and mixtures of the salts and of salts with the investigated spent automotive catalyst. $NaHSO_4 \cdot H_2O$ loses its crystal water in the region 100-310 °C (eq. 1) and decomposes in the region 310-450 °C according to eq. 2, and in the region 600-660 °C according to eq. 3, as described by De Vries and Gellings [16]. For both eq.1 and eq.2 a clear peak in the temperature evolution of water, detected by MS (m=18) was observed, while for eq.3 a small peak related to SO_2 release was seen (see SI).

$NaHSO_4 \cdot H_2O \rightarrow NaHSO_4 + H_2O$ eq. 1

$2NaHSO_4 \rightarrow Na_2S_2O_7 + H_2O$ eq. 2

$Na_2S_2O_7 \rightarrow Na_2SO_4 + SO_3$ eq. 3

$NaClO_3 \rightarrow NaCl + 3/2O_2$ eq. 4

Decomposition of $NaClO_3$ takes place in the region 500-600 °C, according to eq. 4 [17]. During TGA-MS analysis of the catalyst:salt reaction mixture (catalyst: $NaHSO_4 \cdot H_2O$:$NaClO_3$ weight ratio = 1:4.812:0.188) the decomposition reactions of

$NaHSO_4 \cdot H_2O$ were observed as well as the release of small amounts of CO_2 (m=44) (Figure 7).

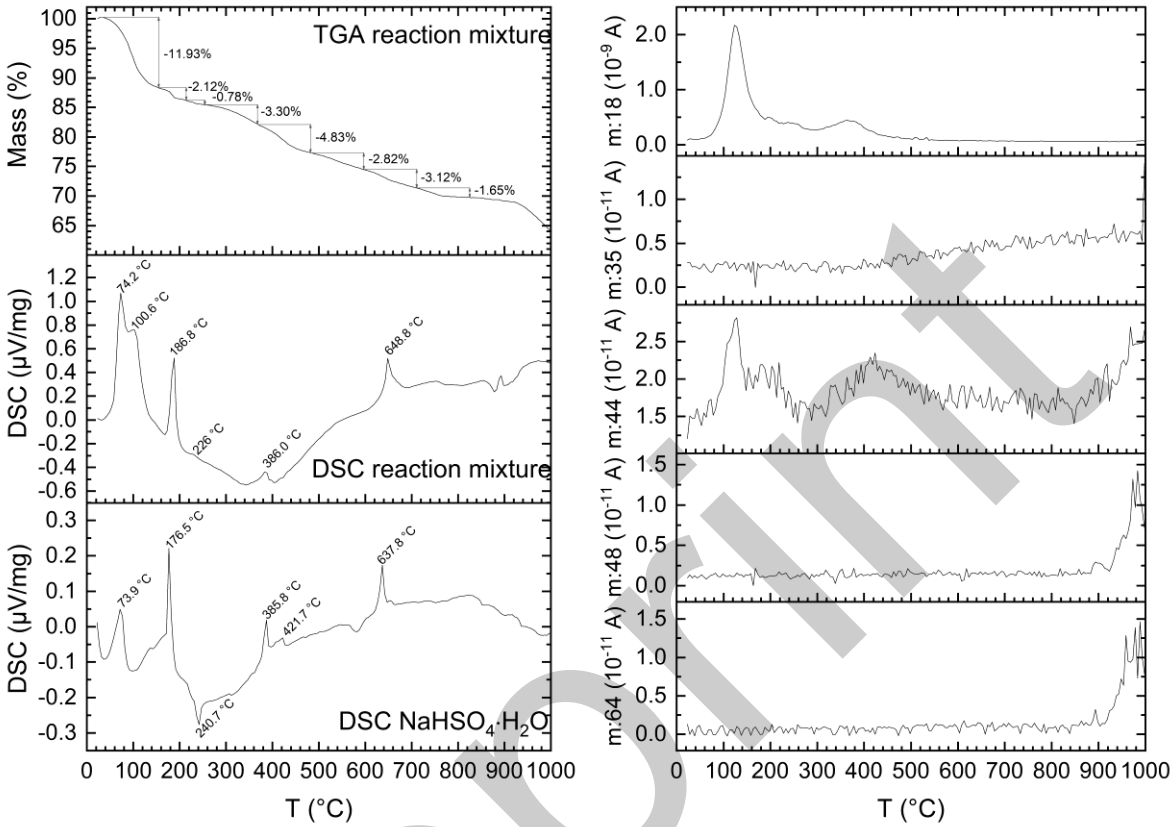

Figure 7: TGA-MS and DSC analyses of a mixture of spent catalyst, $NaHSO_4 \cdot H_2O$ and $NaClO_3$ (respective weight ratio 1:4.182:0.188). Left: TGA and DSC analyses of the mixture and DSC of $NaHSO_4 \cdot H_2O$. Right: MS analyses of the released gasses during TGA of the mixture.

For 42 experiments wherein a sample of spent automotive catalyst was MW roasted with a salt mixture at a salt:catalyst weight ratio of 5 and the salt mixture consisted of a molar ratio of $NaClO_3$:$NaHSO_4 \cdot H_2O$ = 0.05, an average weight loss of 20.3 ±1.8% was measured. A detailed observation of the TGA and DSC measurements of the catalyst:salt mixture shows that the TGA and DSC (Figure 7) profiles agree with those of $NaHSO_4 \cdot H_2O$. Therefore, the mass loss after roasting is mainly related to evaporation of adsorbed water, release of crystal water from $NaHSO_4 \cdot H_2O$ and subsequent decomposition of $NaHSO_4$. According to the TGA profile of the reaction mixture these steps are completed at about 480 °C and account for a total mass loss of

23.0%. Therefore, one can assume that the reaction mixture in a MW furnace at 750 W for 30 min heats to about 480 °C.

Transformations of PGM species during roasting were investigated by XPS analyses of the untreated spent automotive catalyst and roasted catalyst. Weak signals in the XPS spectra (see SI) show that the untreated catalyst contained metallic Pd^0, oxidized Pt^{2+} and Pt^{4+} and metallic Rh^0. Whereas, the roasted catalyst before leaching, contained oxidized Pd^{2+}, oxidized Pt^{2+} and Pt^{4+} and metallic Rh^0. The very weak signals, due to overlap with signals from the cordierite and wash coat elements, did not allow for quantification of the PGM species. These analyses confirm that oxidation of Pd took place that enables better dissolution of the PGM in the subsequent leaching step in which no additional oxidation agent was used.

4 Conclusions

A microwave (MW) sulfation roasting process of the spent ceramic catalyst in the presence of $NaHSO_4{\cdot}H_2O$ and $NaClO_3$, for which the roasting parameters (*e.g.* MW power, roasting time, $NaClO_3$:$NaHSO_4{\cdot}H_2O$ molar ratio, salt:catalyst weight ratio) were studied and optimized. Screening of sulfation agents showed that $KHSO_4$ performed only slightly better than $NaHSO_4{\cdot}H_2O$ and from an economic point of view $NaHSO_4{\cdot}H_2O$ was preferred. Whereas, $NaClO_3$ proved to be the preferred oxidation agent. Although the oxidation agent was required to improve subsequent PGM leachability at a ClO_3^-:HSO_4^- molar ratio of 0.05, an excess addition lowered Pt and Rh leachabilities. For the optimized roasting step a solid mixture of $NaHSO_4{\cdot}H_2O$, $NaClO_3$ and spent catalyst (weight ratio salt:spent catalyst = 5, molar ratio $NaClO_3$:$NaHSO_4{\cdot}H_2O$ = 0.05) was volumetric heated (750 W, 30 min) through absorption of MWs without the use of any other heat source. A range of subsequent leaching tests were tested in water at 60 °C by conventional heating and in water, 0.1 M HCl and 1 HCl solution by MW heating at different temperatures. A design of experiment concluded that the most optimal leaching process took place by MW heating at 105 °C for 30 min in 1 M HCl solution at a liquid to salt ratio of 10. The obtained PGM leachabilities were Pd = 96 ±1%, Pt = 85 ±5% and Rh > 96%. An in depth experimental study of the roasting process showed that sulfation roasting attacks both the cordierite ($Mg_2Al_4Si_5O_{18}$) honeycomb material and rare earth elements, which are present in the wash coat, to form sulfate salts. Some PGMs, Pd in particular, oxidized during roasting that enables better dissolution of the PGMs in the subsequent leaching step in which no additional oxidation agent was applied. Mass loss during

roasting can be ascribed to loss of $NaHSO_4 \cdot H_2O$ hydration water and subsequent decomposition of the sodium sulfate.

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