



Processing of spent platinum-based catalysts via fusion with potassium hydrogenosulfate

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ABSTRACT

This work describes a route for processing spent platinum-based commercial catalysts (Pt and PtSnIn/Al₂O₃) via fusion with potassium hydrogenosulfate (KHSO₄). Samples were previously ground. The optimized experimental parameters were: temperature, 450 °C; time, 3 h; sample/flux mass ratio, 1/10. The fused mass was dissolved in water and the elements present were isolated by a multi-step separation procedure. Platinum was recovered as the only water-insoluble residue. About 45 wt% of aluminium was recovered as KAl(SO₄)₂·12H₂O (alum), whereas the remaining element was recovered as Al(OH)₃. Tin and indium were recovered together as sulfides at pH 1. About 72 wt% of potassium was recovered as K₂SO₄ when the final effluent was treated with sulfuric acid (pH 1) and slowly evaporated. Generation of final wastes was greatly reduced. More than 98 wt% of the elements present in the catalysts examined was recovered.

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1. Introduction

Platinum-group metals (PGM) are widely used in many fields such as catalysts in many chemical processes, electrical and electronic industries, corrosion resistant materials and jewelry [1]. Their excellent selectivity and activity towards reactants and resistance to oxidation at high temperatures make them very effective catalysts. For some of these PGM the demand has not been balanced by supply [2]. PGM are very scarce due to their low natural abundance [3]. Although the amount of these metals in a commercial catalyst is approximately 1 wt%, they correspond to the main cost of this product [4,5]. As most of their rich natural deposits are getting exhausted, the production of PGM from secondary sources (spent catalysts, electronic scrap etc.) has become an important issue [6,7].

Spent catalysts such as petroleum cracking, dehydrogenation, reforming, and hydrogenation ones are classified by the North-American Environmental Protection Agency (EPA) as a hazardous waste since they commonly contain contaminants such as coke, vanadium and nickel [8]. Platinum is commonly found as their active phase. The potentially environmental hazards of spent industrial and automotive catalysts call for putting an emphasis on recovery and recycling policies for these waste materials [9].

Many researches have been performed so as to develop efficient and cost effective recovery methods for PGM [10] from secondary sources. In general, the waste is subjected to strong acidic oxidative leaching resulting in aqueous solutions containing a wide diversity of leached metals, including complex compounds of PGM and also the so-called base metals (BM) [2,7]. Recovery of PGM usually requires numerous unit operations, recycle streams and refining steps [9]. Most processes are costly and require extensive labor and time. Furthermore, large quantities of secondary wastes are generated resulting from the addition of chemical agents for precipitation and reduction in the processes [9].

Solvent extraction (SX) has been widely used for separation of PGM from aqueous solutions [3,11]. This technique offers a number of advantages over the classical precipitation methods due to its higher selectivity. Complete removal of metals is possible through the use of multi-stage extraction [9]. SX has as a major disadvantage large amounts of solvents which are generally toxic for the environment [3]. Its efficiency decreases for the treatment of less concentrated solutions [2].

Sorbents, including ion exchange and chelating resins, may be an alternative to recover small amounts of PGM from solutions containing high amounts of BM, particularly aluminium [3,12–14]. This method is quick, of low cost and offers high efficiency for separation of noble metal ions from many other ions [3,7,12,15]. Anionic ion exchange resins are usually the choice for their recovery [13,16]. However, the sorption recovery of PGM from solutions containing complex compounds of these metals can be complicated, and some valuable compounds may be lost [7]. Another challenge is the des-

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orption step. A common decision is to calcine the resin, leaving the noble metal as an ash residue [7,17].

In recent years, research attention has been focused on biosorption, a biological method which has been demonstrated to possess good potential to replace conventional recovery methods of PGM. Cost effectiveness is the main attraction of metal biosorption [3].

The literature seems to not describe a recovery process based on acid fusion with potassium hydrogenosulfate (KHSO₄) for platinum-based catalysts, which is much less corrosive than the ordinary alkaline fusions (NaOH, Na₂CO₃) cited in the literature [18,19]. In this process amphoteric and basic oxides such as Al, Fe, Mo, Cr and Zn are converted into soluble salts after treatment at high temperatures followed by leaching with water. Since this fusion is a non-oxidative procedure, PGM are expected to be non-reactive, being the insoluble residue in water. The solubilized elements are recovered by conventional precipitation or SX techniques.

In our laboratory spent zeolites [20] and hydrotreating catalysts [21] were successfully treated by acid fusion. Catalyst components were recovered in very good yields (>99 wt%) and final wastes presented low toxicity. In a recent review [22] the acid fusion process has been recognized as a novel route for processing spent catalysts and batteries [23] at least on laboratory scale [22,24]. The support (Al₂O₃) was recovered as aluminium salts. This point is missing in most literature studies [25]. However some remarks were made: (i) the process is high-energy consuming. A study on the optimization of experimental parameters should be performed [26]; (ii) the final effluent is very saline and was generated in considerable quantities [27]; (iii) the excess of flux was entirely lost in the final effluent [27,28]. Based on these remarks the main improvements in the acid fusion process are: (i) to reduce the energy consumption; (ii) to recover at least partially the flux present in the final effluent.

This work aims at describing a new process (acid fusion) to recover valuable elements present in spent platinum-based catalysts. The influence of reaction time, temperature and catalyst/flux mass ratio was investigated. The insoluble matter obtained after treatment of the fused mass with water was characterized and leached elements were recovered by a combination of precipitation and crystallization techniques. Attention was attracted to the final wastes generated.

2. Experimental

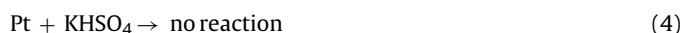
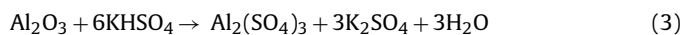
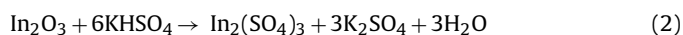
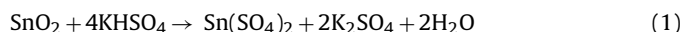
2.1. Catalysts

Two spent commercial platinum-based catalysts were employed in this study: Pt/Al₂O₃ and PtSnIn/Al₂O₃. Samples were used in Brazilian refineries. Chemical analyses are presented in Table 1. The catalysts were ground in a ball mill. All samples presented particle size below 0.147 mm (>100 mesh).

2.2. Fusion process

The flux employed was potassium hydrogenosulfate (KHSO₄, m.p. 214 °C), which is converted into potassium pyrosulfate (2KHSO₄ → K₂S₂O₇ + H₂O) at somewhat higher temperatures. The latter is the effective reactant during fusion. The stoichiometric amount of flux necessary to the process was calculated according

to the following reactions:



The theoretical catalyst/flux mass ratio is 1:8 for both samples. It is expected to recover platinum as the insoluble matter in water since this fusion is a non-oxidative process. The progress of the fusion was monitored by the amount of the insoluble matter found after each experiment.

Experiments were carried out in 1–10 g scale. After mixing the sample with the flux (catalyst/flux mass ratio 1:5, 1:10 or 1:15) the crucible was placed in a furnace at a given temperature (350–550 °C, 4 °C min⁻¹) for a given time (1–6 h). Fusion was performed under air in order to avoid any reduction of sulfate to SO₂ and/or sulfide species, which would form insoluble compounds (such as SnS₂, In₂S₃ and PtS). During fusion the gaseous effluent was washed down with distilled water (10 °C) to recover any SO_x produced. The roasted mass was cooled down in the furnace and leached with distilled water at 90–100 °C for 30 min and stirring at 200 rpm. The solid residue was separated from the liquid phase by centrifugation and washed with water (5 mL g⁻¹ solid). This procedure was performed three times in order to eliminate SO₄²⁻ and K⁺ ions. The washed solid was dried at 150 °C for 3 h and weighed. The leachate was employed for metals recovery. The experiments were run in triplicate, and errors for each experiment were always below 3%.

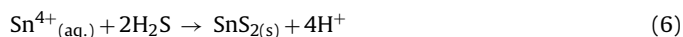
2.3. Recovery of leached elements

2.3.1. Crystallization of alum (KAl(SO₄)₂·12H₂O)

The basis of this process is its lower solubility in water (114 g L⁻¹ at 20 °C) when compared to Al₂(SO₄)₃·18H₂O (869 g L⁻¹ at 20 °C) and K₂SO₄ (120 g L⁻¹ at 20 °C) [29]. The leachate was left to stand at 25 °C for 1–48 h. The crystallized solid was filtered and washed with ethanol + water (1:1, v/v) at 10 °C (3 mL g⁻¹ alum) and dried under vacuum before weighing.

2.3.2. Precipitation of tin and indium

After alum recovery, these metals were isolated as sulfides by adding dropwise 1 mol L⁻¹ Na₂S under stirring (200 rpm) at 90 °C:



The brown solid was centrifuged, washed two times with water (3 mL g⁻¹) and dried at 150 °C for 3 h.

2.3.3. Recovery of remaining aluminium

6 mol L⁻¹ KOH was added dropwise at 25 °C (200 rpm) until pH around 6.5. The white precipitate (Al(OH)₃) was filtered, washed with 0.01 mol L⁻¹ NH₄NO₃ (5 mL g⁻¹) and water (3 mL g⁻¹), and dried 110 °C for 3 h.

2.3.4. Recovery of flux

The final effluent was acidified with 10 mol L⁻¹ H₂SO₄ until pH 1. This pH is typical of aqueous KHSO₄ solutions [29,30]. The use

Table 1
Chemical analysis (wt%, dry basis) of the spent catalysts.

	Pt	Sn	In	Al	Fe	C
Pt/Al ₂ O ₃	0.35	–	–	52.80	0.02	3.5
PtSnIn/Al ₂ O ₃	0.39	0.42	0.28	50.82	0.03	5.0

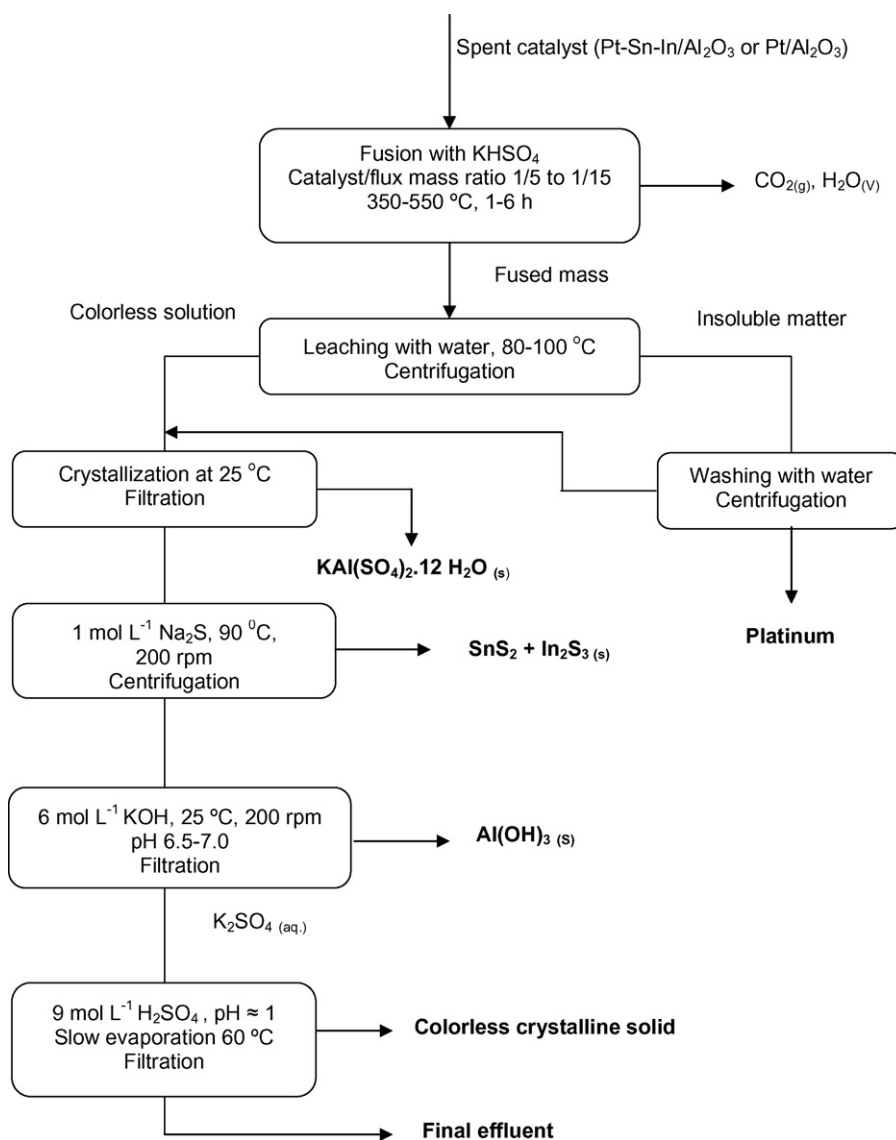


Fig. 1. General scheme for recovery of Pt, Al, Sn and In after catalyst fusion with KHSO₄ and leaching the fused mass in water.

of KOH to precipitate the remaining soluble aluminium avoided introduction of foreign cations (such as Na⁺). No crystallization took place after adjusting pH. Therefore the acidic solution was slowly evaporated at 60–70 °C (without stirring). After this step the new solution was cooled in an ice bath. The white solid was filtered, washed three times with ethanol (3 mL g⁻¹) and dried at 25 °C. Fig. 1 presents the overall scheme for processing the metals in the leachate

2.4. Analytical methods

The insoluble matter in water after fusion and the final products obtained in the separation step were weighed in an analytical balance (Scientech SA 120). Metal concentrations in the leachates were determined by atomic absorption spectrometry (Perkin Elmer AAS 3300). The following wavelengths were employed: platinum, 265.9 nm; tin, 286.3 nm; indium, 303.9 nm; aluminium, 396.2 nm; potassium, 766.5 nm. The following detection limits were determined experimentally: 1 mg L⁻¹ (aluminium, potassium and tin), 0.5 mg L⁻¹ (indium and platinum). The solids were dissolved in water (alum and the white solid), HCl 1 mol L⁻¹ (Al(OH)₃) and aqua regia (insoluble matter in water after fusion and In₂S₃ + SnS₂). Acid-

ity was determined by potentiometry using an Ag/AgCl reference electrode (Orion 2A13-JG). Crystalline phases in the solid samples were identified by X-ray diffraction analysis (Shimadzu model XRD 6000) by continuous scanning method at 20 mA and 40 kV, using Cu Kα as the radiation source.

3. Results and discussion

3.1. Effect of the catalyst/flux mass ratio

In general, the fusion conducted near the stoichiometric sample/flux mass ratio is a slow process and it risks to loose yield due to losses of flux (decomposition, side reactions etc.) [19]. Therefore the normal procedure is to use an excess of flux so as to compensate such losses and to accelerate the fusion kinetics.

The experiments were accomplished at 400 °C. The catalyst/flux mass ratios tested were 37.5 wt% lower and 25 and 90 wt% higher than the stoichiometric value for both samples (1:8, w/w). The results are presented in Fig. 2.

Fusion below the stoichiometric mass ratio was a very slow process and the amount of insoluble matter in water was much higher since there was no enough flux to react with the sample. The pos-

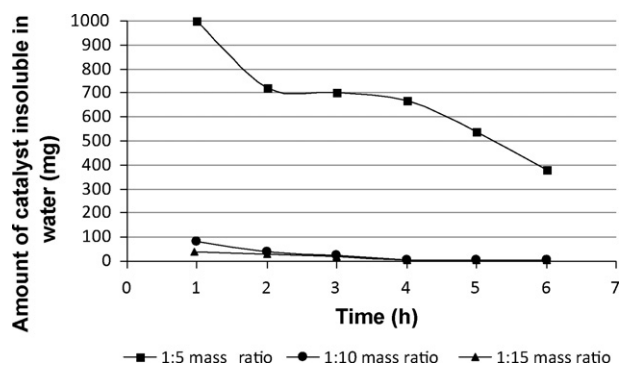


Fig. 2. Effect of the catalyst/flux mass ratio on fusion process with KHSO_4 of the $\text{PtSnIn}/\text{Al}_2\text{O}_3$ catalyst at 400°C (1 g sample).

itive effect of excess of flux is clear when the ratio varied from 1:5 to 1:10. Ratios above 1:10 served no advantage (differences lower than 5%). For both ratios (1:10 and 1:15) the time necessary to reach a final behavior was 4 h. The optimum catalyst/flux mass ratio found in this work was also the best ratio found for processing spent hydrotreating (CoMo and $\text{NiMo}/\text{Al}_2\text{O}_3$) catalysts [21]. However it must be emphasized that the best sample/flux mass ratio depends on the amount of sample that reacts with the flux (KHSO_4 , in the present case). As the amount of non-reactive species in a given sample increases the sample/flux mass ratio also increases as less flux is necessary to treat the sample [20–22].

3.2. Effect of temperature

In this study fusion was conducted in the range of 350 – 550°C , using a catalyst/flux mass ratio 1:10. The results are presented in Fig. 3 for the $\text{PtSnIn}/\text{Al}_2\text{O}_3$ catalyst.

Fusion at 350°C presented a peculiar behavior when compared to the experiments carried out at higher temperatures. After 4 h a final insoluble matter in water was obtained but its amount is ten times greater than at 400°C . In this case a considerable portion of coke remained in the insoluble residue since it was not reactive towards the flux. This explains why the amount of insoluble matter in water after fusion at 350°C is much higher than for other temperatures, where carbon was eliminated from the samples. The progress of slower fusion at 350°C is a combination of kinetic factors and accessibility of the flux to some reactive matter (occluded by coke).

The experiments at 400 and 450°C presented a very similar behavior. The insoluble matter corresponds to less than 0.05 wt% of the original catalyst mass. The only difference was the time to reach the final behavior: 3 h (450°C) and 4 h (400°C). Longer times did not present any influence of fusion behavior.

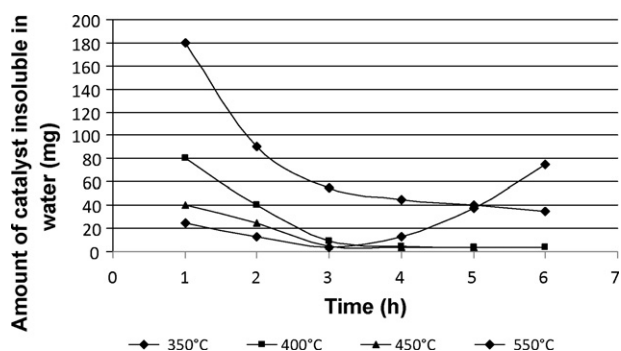


Fig. 3. Effect of temperature the fusion of the $\text{PtSnIn}/\text{Al}_2\text{O}_3$ catalyst with KHSO_4 (catalyst/flux mass ratio 1:10, 1 g sample).

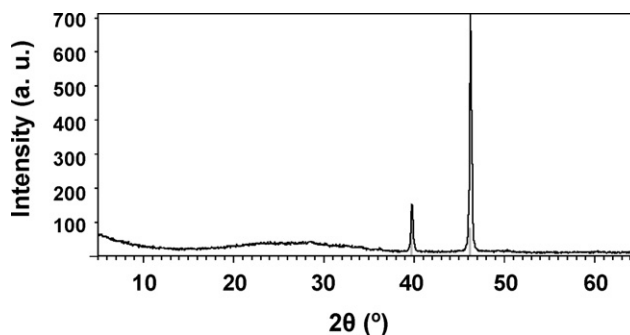


Fig. 4. X-ray diffractogram of the insoluble residue in water of the $\text{PtSnIn}/\text{Al}_2\text{O}_3$ catalyst after fusion with KHSO_4 at 450°C for 6 h (catalyst/flux mass ratio 1:10).

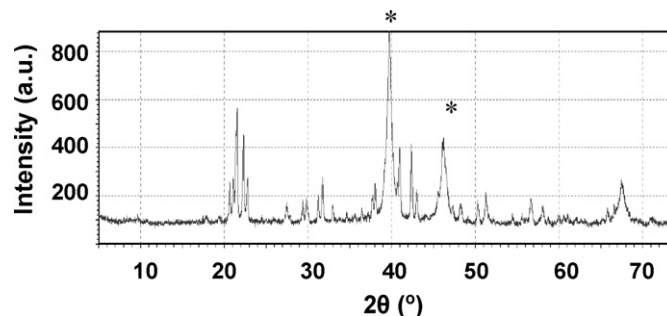


Fig. 5. X-ray diffractogram of the insoluble residue in water of the $\text{PtSnIn}/\text{Al}_2\text{O}_3$ catalyst after fusion with KHSO_4 at 550°C for 6 h (catalyst/flux mass ratio 1:10) (peaks assigned with an *: platinum).

Fusion at 550°C presented an initial behavior identical to the experiment carried out at 450°C . However after 3 h the amount of insoluble matter in water tended to increase with time. Anyway, it is also clear that fusion at 450°C for 3 h is the choice because of the lower energy consumption. This result is an advantage of the acid fusion process over the common alkaline fusions [18,19], which require temperatures over 500°C (NaOH) or 850°C (Na_2CO_3) for their effectiveness. The optimum time and fusion temperature found in this study are in the same range as in previous studies [20,21]. However, it must be pointed out that the principal reactive part of all catalysts employed was the same ($\gamma\text{-Al}_2\text{O}_3$).

The insoluble residue after fusion at 450°C (3 h) and 550°C (6 h) were analyzed by X-ray diffraction. Only platinum peaks were observed in the diffractogram of the solid after fusion at 450°C (Fig. 4). Its mass ($3.67 \pm 0.04 \text{ mg g}^{-1}$ catalyst) agrees very well with the amount of noble metal present in the multimetallic catalyst (Table 1). This result confirms that platinum can be the only insoluble matter in the acid fusion process. The diffractogram of the insoluble matter after fusion at 550°C for a long time (Fig. 5) presents platinum peaks (assigned with *) and also many new peaks. It was not possible to identify the new crystalline phases formed. For this reason the chemical analysis of this solid was of utmost importance. Data are presented in Table 2.

These data show that the other catalyst components are present in this solid, thus suggesting the occurrence of reactions involving these components forming insoluble compounds (such as spinels

Table 2

Metals composition (wt%) of the insoluble matter in water after fusion of $\text{PtSnIn}/\text{Al}_2\text{O}_3$ catalyst with KHSO_4 (450 or 550°C) during 6 h (sample/flux mass ratio 1:10).

Temperature ($^\circ\text{C}$)	Pt	Sn	Al	In
450	>99.9	<0.1	<0.1	<0.1
550	34	6	54	6

and mixed oxides [31,32]). This result makes direct platinum recovery impossible. Therefore, the acid fusion must be conducted under controlled experimental conditions in order to avoid undesirable side reactions.

The optimal experimental parameters for the Pt/Al₂O₃ catalyst are identical to the multimetallic sample. The only difference is the absence of additional insoluble matter in the experiments at 550 °C for more than 3 h. This result is ascribed to the absence of other metals in the sample under study. Platinum is the only insoluble matter in these circumstances.

The pH was in the range 0.8–1, which was acid enough to avoid precipitation of tin. This is basically due to its low amount in the multimetallic catalyst (Table 1). Sn⁴⁺ ion is subjected to an extensive hydrolysis, precipitating tin in acidic pH [29,30]. In this situation tin would contaminate the noble metal.

3.3. Metals recovery

3.3.1. Platinum recovery

Fusion under adequate experimental conditions leads to platinum as the only insoluble matter in water. Its purity (Table 2; Fig. 4) is very good (Section 3.2). However, it must be emphasized the importance of the washing step of crude platinum (Section 2.3) in order to reach the high purity grade of the final product. The amount recovered corresponds to more than 99.5 wt% of the noble metal present in the samples processed. Direct platinum recovery from the other catalyst components is an advantage of the acid fusion process. Platinum recovery in most processes cited in the literature [2,7,9,22,33] requires several steps in order to separate it from the other catalyst components.

3.3.2. Aluminium recovery as alum

The amount of recovered alum is directly dependent on the amount of water used to dissolve the fused mass. During platinum recovery the temperature decreases. Therefore, crystallization of alum must begin after platinum recovery. Otherwise co-crystallization would reduce alum yield and increase water consumption when washing crude platinum. On the other hand an excessive amount of water reduces alum recovery. For these reasons a study on the influence of amount of water for leaching the fused mass on alum yield was performed. The established criterion was to determine the minimum amount of water where alum does not co-crystallize with platinum. The volumes tested were in the range 50–100 mL. The minimum volume of water to accomplish this objective was 80 mL g⁻¹ sample for both catalysts. In this situation the alum yield is the highest. Taking into account the amount of flux and the catalyst employed in the experiments (10 g and 1 g, respectively) and the catalyst composition (Table 1), the concentrations in this solution are: [Al³⁺] ≈ 0.23 mol L⁻¹; [K⁺] and [SO₄²⁻] ≈ 0.92 mol L⁻¹. These values are in the range employed for alum industrial synthesis [34,35]. pH of the solution (0.8–1) is only slightly below the optimum range found in the literature (1–2) [30,35]. For this reason pH was not adjusted for alum recovery.

Standing for more than 24 h did not increase significantly the mass of alum recovered (4.03 g g⁻¹ sample for both catalysts).

It is not advisable to evaporate the solution after platinum recovery. Under heating (even without stirring) the Al³⁺ ion is subjected to hydrolysis, thus reducing yield and purity of alum [30].

Indium (present in the multimetallic sample) also forms double sulfates as aluminium [29,30]. However, since this metal is present in very low amounts in the multimetallic catalyst, crystallization of KIn(SO₄)₂·12H₂O does not take place.

Fig. 6 presents the diffractogram of the alum recovered. It agrees very well with the pattern of this compound. Its aluminium content is 5.71 wt% (theoretical value 5.70 wt%), whereas potassium com-

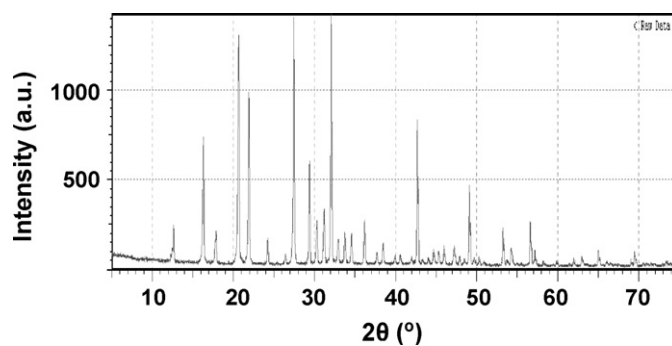


Fig. 6. X-ray diffractogram of the alum (KAl(SO₄)₂·12H₂O) crystallized at 25 °C for 24 h after fusion of the PtSnIn/Al₂O₃ catalyst with KHSO₄ at 450 °C for 3 h (catalyst/flux mass ratio 1:10). The fused mass was dissolved in 80 mL of water.

prises 8.18 wt% of the solid (theoretical value 8.23 wt%). Thus the alum recovered presents a very high purity grade.

Based on the stoichiometry 1Al³⁺ (27 g) = 1KAl(SO₄)₂·12H₂O (474 g) and the aluminium content of the spent catalysts (Table 1) the theoretical masses of alum per g of sample processed are: 8.92 g (PtSnIn/Al₂O₃) and 9.27 g (Pt/Al₂O₃). Since the experimental amount of alum recovered was 4.03 g (for both samples), the amount of this compound recovered was 45.3 wt% (PtSnIn/Al₂O₃) and 43.6 wt% (Pt/Al₂O₃).

Aluminium sulfate (Al₂(SO₄)₃·18H₂O) has replaced alum in most industrial applications, specially for water treatment. However alum is still used in tannery, pharmaceutical, clothing and cosmetic industries, as well as for latex coagulation and additive for cement and plaster manufacturing [34,35].

3.3.3. Recovery of tin and indium

These elements are present in very low amounts in the leachate of the multimetallic catalyst (40–45 mg L⁻¹, 0.36–0.37 mmol L⁻¹). Their sulfides (SnS₂ and In₂S₃) were quickly precipitated (5–8 min) after adding only 4–5 drops of 1 mol L⁻¹ Na₂S. The mass of the solid obtained was 11.9 mg. The theoretical mass of both sulfides based on the metal amounts found in Table 1 is 10.4 mg g⁻¹ catalyst. The experimental mass is 15% higher. Chemical analysis of this solid indicates that it contains 98.5 wt% of indium and 99 wt% of tin present in the sample processed. No attempt was made to separate these metals.

The diffractogram of the solid indicates it is poorly crystalline. The small peaks correspond to elemental sulfur. This result explains the higher experimental mass when compared to the theoretical one for the mixture of the two sulfides.

3.3.4. Recovery of the remaining soluble aluminium

The average amount of 6 mol L⁻¹ KOH added to precipitate the remaining soluble aluminium by adjusting pH from 0.8–1 to 6.5–7 was 17 mL.

The mass (weighed as Al(OH)₃) was 800 ± 2 mg (PtSnIn/Al₂O₃) and 852 ± 3 mg (Pt/Al₂O₃). Aluminium corresponds to >99.7 wt% of all metals present. The other metal found was iron (it is present in small amounts in both catalysts – Table 1). Washing of this precipitate is essential to remove SO₄²⁻ and K⁺ ions, thus ensuring a high purity aluminium final product.

3.3.5. Analysis of the crystallized solid

The initial volume of final effluent is about 100 mL g⁻¹ processed catalyst. The initial volume (leaching the fused mass) was 80 mL. Precipitation of tin, indium and aluminium and pH adjustment of the final effluent increased this volume.

As expected, the mass of the solid recovered increased as the amount of water evaporated increased. Traces of aluminium

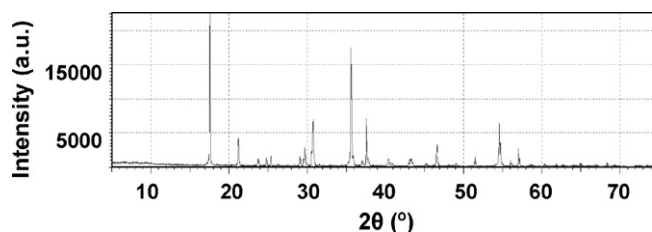


Fig. 7. X-ray diffractogram of the solid recovered after slow evaporation of the final effluent (pH 1). The peaks represent potassium sulfate (K_2SO_4).

(0.01 wt%) were found when more than 50 vol.% of the effluent was evaporated. Therefore evaporation was stopped at this point. Under these circumstances the mass of the solid recovered was 5.34 g g^{-1} catalyst.

Potassium comprises >99.9 wt% of the metals present in the solid and 44.9 wt% of the solid itself. This last result indicates the solid crystallized is K_2SO_4 (44.83 wt% K^+) and not $KHSO_4$ (28.7 wt% K^+). The diffractogram of this solid (Fig. 7) shows a very crystalline solid and the peaks correspond to K_2SO_4 . This result is a clear reflection of the different solubilities of the two salts in water: $KHSO_4$ is much more soluble in water (490 g L^{-1} at 20°C) than K_2SO_4 (120 g L^{-1} at 20°C). The alternative to convert K_2SO_4 into $KHSO_4$ was to add the stoichiometric amount of concentrated H_2SO_4 to the solid at 25°C . $KHSO_4$ crystals were formed [34,35]:



3.4. Mass balance for aluminium

The amount of aluminium recovered as alum was 45.3 wt% ($PtSnIn/Al_2O_3$) and 43.6 wt% (Pt/Al_2O_3) since the stoichiometry is 1:1 (w/w) ($1Al^{3+} = 1KAl(SO_4)_2 \cdot 12H_2O$).

The other final aluminium product is its hydroxide. Based on the stoichiometry $1Al^{3+} = 1Al(OH)_3$ and the masses of the hydroxide ($800 \pm 2 \text{ mg}$ for $PtSnIn/Al_2O_3$ and $852 \pm 3 \text{ mg}$ for Pt/Al_2O_3), the masses of aluminium recovered were 0.277 g (54.4 wt% – $PtSnIn/Al_2O_3$) and 0.295 g (56.0 wt% – Pt/Al_2O_3). Therefore, the overall aluminium recovered was 99.7 wt% ($PtSnIn/Al_2O_3$) and 99.5 wt% (Pt/Al_2O_3). This result is comparable to literature data [18,25–27,33]. However, in this study, lower amounts of strong base (KOH) and water were necessary to precipitate soluble aluminium. This result is of environmental interest and due to partial recovery of the element as alum.

3.5. Mass balance for potassium

Based on the mass of alum recovered (4.03 g g^{-1} catalyst) and the stoichiometry $1K^+ = 1KAl(SO_4)_2 \cdot 12H_2O$, this mass contains 0.332 K^+ ions. 10 g of $KHSO_4$ contain 2.87 g K^+ . Therefore, 11.6 wt% of potassium was recovered in the alum for both catalysts. The other potassium final product is K_2SO_4 ($1K_2SO_4 = 2K^+$). The amount of potassium in the leachate comes from the flux (2.87 g) and the 6 mol L^{-1} KOH added to precipitate soluble aluminium ($17 \text{ mL} - 0.312 \text{ g K}^+$): 3.182 g. The mass of K_2SO_4 recovered (5.34 g g^{-1} catalyst) contains 2.39 g K^+ (72.3 wt%). The overall K^+ recovery was $11.6 + 72.3 = 83.9 \text{ wt}\%$.

3.182 g K^+ corresponds to 7.10 g of K_2SO_4 . Thus, the yield of this salt was $5.34/7.10 = 75.2 \text{ wt}\%$. The main loss of K^+ ions is the due to partial crystallization of K_2SO_4 as stated by the purity criterion established earlier.

The partial recovery of K_2SO_4 is an important issue. The flux can be prepared from this salt and the final effluent will be less saline.

3.6. Final wastes management

The final effluent after K_2SO_4 recovery was neutralized with 6 mol L^{-1} KOH. This is the only final waste and it meets the requirements for disposal according to the Directory 357 from the National Brazilian Environmental Council [36].

About 50 mL of final neutralized waste were generated per g of catalyst. The main reason for this result is the minimum volume of water necessary to dissolve the fused mass (80 mL) so as to avoid partial co-crystallization of alum with platinum. This result is better than our previous results [20,21], where about 90 mL g^{-1} sample were generated. This is due to recovery of K_2SO_4 .

4. Conclusions

The fusion of spent Pt and $PtSnIn/Al_2O_3$ catalysts with $KHSO_4$ allowed a very good overall metals recovery (>99.5 wt%). The process itself required less drastic experimental conditions when compared to the classical pyro/hydrometallurgical processes. It is not necessary to use more than 25 wt% excess of the stoichiometric amount of flux to accomplish the fusion under a reasonable time.

The optimum fusion temperature is 450°C , where the insoluble matter corresponds only to platinum. Direct platinum recovery is an advantage of the acid fusion process. Under these circumstances the time of fusion was 3 h.

Alum recovery depends on the amount of water employed to dissolve the fused mass. 80 mL was the minimum volume where platinum can be recovered without partial alum co-crystallization. Alum recovery reduces consumption of strong base and water to precipitate soluble aluminium. This element, tin and indium were recovered in very good yields (>98 wt%).

Recovery of more than 70 wt% of K_2SO_4 allowed synthesis of the flux and greatly reduced the salinity of the final effluent.

The final wastes produced present low toxicity. Their composition is much simpler than those found in many processing routes of spent materials found in the literature [22].

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