Journal of Hazardous Materials

Short communication

Processing of spent NiMo and CoMo/Al$_2$O$_3$ catalysts via fusion with KHSO$_4$

Roberto Giovanini Busnardo, Natália Giovanini Busnardo,
Gustavo Nascimento Salvato, Júlio Carlos Afonso *

*Analytical Chemistry Department, Institute of Chemistry, Federal University of Rio de Janeiro, P.O. Box 68563,
21949-900 Ilha do Fundão, Rio de Janeiro, Brazil*

Abstract

This work describes a route for processing spent commercial hydrorefining (HDR) catalysts (CoMo and NiMo/Al$_2$O$_3$), containing support additives, for recovering active phase and support components. Samples were used as catalysts in diesel hydrotreaters. They had neither been submitted to mechanical stresses nor overheating while under operation. The route is based on fusion of samples with KHSO$_4$. Four experimental parameters were optimized: reaction time, sample/flux mass ratio, temperature, and sample physical characteristics (ground/non-ground). After fusion, the solid was dissolved in water (90–100 °C); the insoluble matter presented low crystallization. Several phases were identified: silicates, spinel-like compounds and aluminosilicates. Cobalt, nickel, molybdenum and aluminum were recovered by conventional precipitation techniques or selective solvent-extraction procedures, with at least 85 wt.% yield. Final liquid colorless effluents are obtained as neutral solutions of alkali sulfates or chlorides and a water insoluble solid after fusion, which can be either sent to industrial dumps or co-processed. Fusion with KHSO$_4$ was shown to be applicable to the catalysts of the present study, and the optimized experimental parameters are much less drastic than the conventional pyrometallurgical routes proposed in the literature.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Spent catalyst; Metals recovery; Hazardous waste

1. Introduction

During the 1990s more than 130 new catalysts or improved samples were introduced only in the United States in preexisting or new catalytic processes [1]. This demonstrates that catalyst technology will continue to play a central role in the modern industry but also the spent catalyst will become a more complex challenge to the owners of such samples. The increasing severity of the environmental legislations has forced the treatment of spent catalysts to give a reasonable final destination. Since there are many types of catalysts under a very wide composition range, each spent sample is a case study in order to determine the best final destination. The treatment method depends on the local environmental legislation, market and available technologies [2].

Spent catalyst generation has rapidly been increasing worldwide. In the United States the amount raised by 25 wt.% [3] in the period of 1992–2000. The petroleum refinery industry has received much attention in recent years. The processing of feedstocks containing high nitrogen, sulfur and metal contents and the demand for low-sulfur fuels (thus requiring a deeper hydrorefining (HDR) capacity) has increased [4]. Spent refinery catalysts typically correspond to 4 wt.% of the overall waste [5] but are among the most dangerous materials [6] to the environment. Such spent materials have been classified as a hazardous material [7] by the environmental protection agency (EPA), as they may release toxic gases, are subjected to spontaneous ignition and contain components that pollute the environment (heavy metals and polyaromatic compounds). The hazard depends on the feedstock treated: the more it is heavier, the more dangerous the spent catalyst will be [7,8].

Since a spent HDR catalyst is a multi-component sample, its previous characterization is necessary to determine its final destination (recycling, regeneration, metals recovery or disposal)

* Corresponding author. Tel.: +55 21 2562 7555; fax: +55 21 2562 7892.
  E-mail address: julio@iq.ufrj.br (J.C. Afonso).

[9]. In Brazil the most current final destination is co-processing, provided the co-produced cement keeps its pozzolanic properties and does not exhibit toxicity during its handling [10].

Metals recovery from spent HDR catalysts presents some interesting advantages: (i) the amount of Ni, Co and Mo normally surpasses those found in ores [11]; (ii) the market value of those metals, cobalt in particular, has been increasing in the last 5 years; (iii) the cost of Ni, Co and Mo is more than 30% of the catalyst [12]. In the last 10 years the interest on recovering metals from spent catalysts has risen due to its environmental and economical benefits [4]. Additionally, as the cost for storing and disposing spent catalyst tends to rise, the recovery procedure becomes a viable solution [4]. In fact, metals recovery reduces the catalyst cost and also the environmental pollution provided the final wastes are less toxic than the original materials [13]. Many new processes have been proposed, not only based on environmental advantages (lower energy consumption, less final waste generation, etc.), but also on high yields on metals recovery or selective recovery of a specific element. Among these new processes, attention has been attracted to bio-hydrometallurgical routes for processing spent HDR catalysts since they can be performed under very mild experimental conditions, offering low cost and energy requirements, are environmentally safe and present a good operational flexibility [14,15]. *Aspergillus niger* is one of the most used microorganisms. Oxalic acid is the major leaching agent produced by fungi [14]. The yields were moderate (54–82 wt.%) but the process took a long while (30–60 days). Roasting of a spent NiMo catalyst with NaCl (900 °C) [2] is suitable for selectively recovering Mo, but other elements require further steps in order to be recovered. Leaching with inorganic acids (sulfuric acid in particular) is the most common method for metals recovery [16]. The yields may surpass 99 wt.% but elements such as Si must be absent since their compounds are not attacked by acid leaching (except HF [17]). Silicon is usually found as a support additive and can be deposited on the catalyst surface during its use should the feedstock contains this element.

The literature seems to not describe a recovery process based on acid fusion with potassium hydrogen sulfate ($KHSO_4$), which is much less corrosive than the ordinary alkaline fusions (NaOH, Na_2CO_3). In this process Mo, Al, Co and Ni are converted into soluble salts after treatment at high temperatures followed by dissolution in water. Si and P are obtained as insoluble residues. The solubilized elements are recovered by conventional precipitation or solvent-extraction techniques [18]. In general, aluminum recovered is co-processed or employed as a raw material for aluminum sulfate production [19].

This work aims at describing a new recovery process of valuable elements present in spent HDR catalysts. The influences of catalyst particle size, reaction time, temperature and catalyst/flux mass ratio were investigated. The insoluble matter obtained after treatment of the fused mass with water was characterized and solubilized elements were recovered by a combination of precipitation and solvent-extraction techniques. Attention was attracted to the final wastes generated.

Table 1
Chemical analysis (wt.%, dry basis) and some physicochemical properties of the spent HDR catalysts

Sample	Ni or Co	Mo	Fe	Al	P	S	C	Si
NiMo	2.1	9.5	0.7	31.8	0.5	3.1	10.0	<0.1
CoMo	2.5	9.9	0.9	32.6	2.0	3.4	11.9	2.9

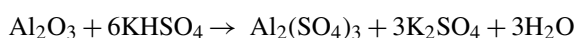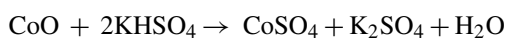| Sample	Surface area (m² g⁻¹)		Pore volume (mL g⁻¹)
NiMo	88		0.065
CoMo	76		0.045

2. Experimental

2.1. Catalyst

The NiMo and CoMo catalysts (5 mm cylinder extrudates) employed in this study came from Brazilian refineries for HDR of diesel fractions. Chemical analyses (and other physicochemical properties) are presented in Table 1. They were partially ground and the <0.147 mm fraction (>100 mesh) was used. Samples were dried at 110 °C for 2 h.

2.2. Fusion process

The flux employed was potassium hydrogen sulfate ($KHSO_4$, mp 214 °C), which was converted into potassium pyrosulfate ($2KHSO_4 \rightarrow K_2S_2O_7 + H_2O$) 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:

$$NiO + 2KHSO_4 \rightarrow NiSO_4 + K_2SO_4 + H_2O$$

$$CoO + 2KHSO_4 \rightarrow CoSO_4 + K_2SO_4 + H_2O$$

$$Al_2O_3 + 6KHSO_4 \rightarrow Al_2(SO_4)_3 + 3K_2SO_4 + 3H_2O$$

$$MoO_3 + 2KHSO_4 \rightarrow MoO_2SO_4 + K_2SO_4 + H_2O$$

thus giving a theoretical catalyst/flux mass ratio of 1:5 for both samples. It is expected to recover silicon (SiO_2) and phosphorus (phosphate-bearing species) as insoluble matter. Thus, 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 the crucible was placed in a furnace at a given temperature (350–600 °C, 4 °C min⁻¹) for a given time (0.5–7 h). Fusion was performed under air in order to avoid any reduction of sulfate to SO_2 and/or sulfide species, which would form insoluble compounds (such as NiS and MoS_2). During fusion the gaseous effluent was washed down with distilled water (10 °C) to recover any SO_x produced. This solution was used to determine the amount of flux lost in this way (precipitation as $BaSO_4$ by addition of $BaCl_2$ (1 mol L⁻¹)). The roasted mass was cooled down in the furnace and leached with distilled water at 90–100 °C for 40 min and stirring at 200 rpm. The solid residue was separated from the liquid phase by filtration, washed with

water (5 mL g^{-1} of solid), dried at 110 °C for 2 h and weighed. The solution was employed for metals recovery. The pH was in the range of 1–2, which did not allow the precipitation of solubilized P. The experiments were run in triplicate, and errors for each experiment were always below 3%. The solid residue was dissolved in HF + HCl (1:1 (v/v)) at 60 °C for further analysis.

2.3. Analytical methods

Metal concentrations were determined by atomic absorption spectrometry (solutions) or X-ray fluorescence (solids). Sulphate, fluoride and phosphate ions were determined by ion-chromatography. Carbon and sulphur contents were determined by a LECO analyser. Crystalline phases in the solid samples were identified by X-ray diffraction analysis.

3. Results and discussion

3.1. Effect of catalyst grinding

Both ground and non-ground samples were treated at 350 °C with some catalyst/flux mass ratios. Data are presented in Fig. 1. As expected, the previous grinding speeded up the fusion process, which takes about 4–5 h (depending on the sample), whereas non-ground samples takes longer to accomplish that process.

The amount of insoluble matter in the equilibrium state (20–30 wt.% according to the sample) surpasses the amount of coke deposited on the surface (10–11 wt.%, Table 1). This is ascribed to the presence of non-reactive compounds (Si and P

ones) as well as some reactive phases occluded by coke. The samples after fusion did not present the characteristic odor of organic compounds as observed in the original spent catalysts as the volatile fraction was eliminated during the treatment. For the sequence of the experiments only ground samples were employed.

3.2. 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.) [20]. 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 350 °C with the ground samples. The catalyst/flux mass ratios tested were 50, 100 and 150% higher than the stoichiometric value for both samples (1:5 w/w). The results are presented in Fig. 2.

The positive effect of excess of flux is clear when the ratio varied from 1:7.5 to 1:10 (the amount of insoluble matter in water after the process decreased about 25 wt.%). Ratios above 1:10 served no advantage. On the other hand, the necessary time to reach a final behavior is essentially the same for each sample (4 h: CoMo and 5 h: NiMo) for both 1:10 and 1:15 ratios.

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

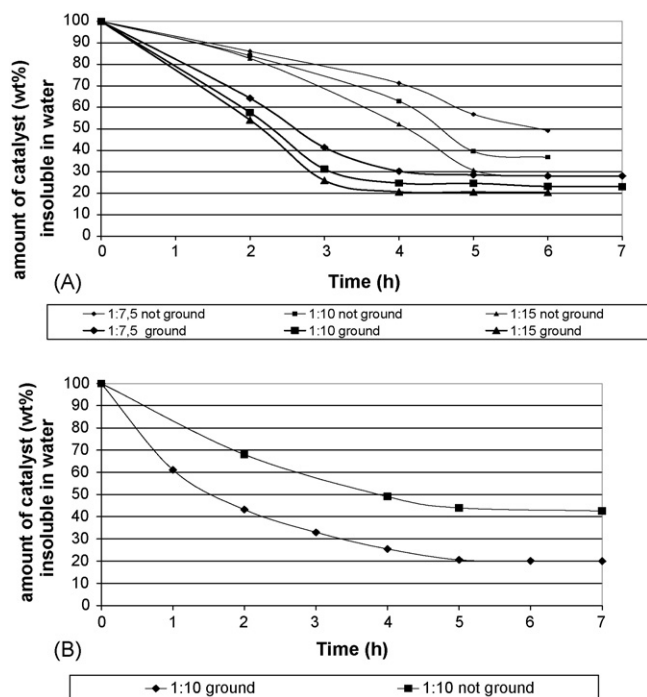Fig. 1. Effect of grinding of CoMo (A) and NiMo (B) catalysts on the fusion process with KHSO$_4$ (350 °C, catalyst/flux mass ratio 1:7.5, 1:10 or 1:15).

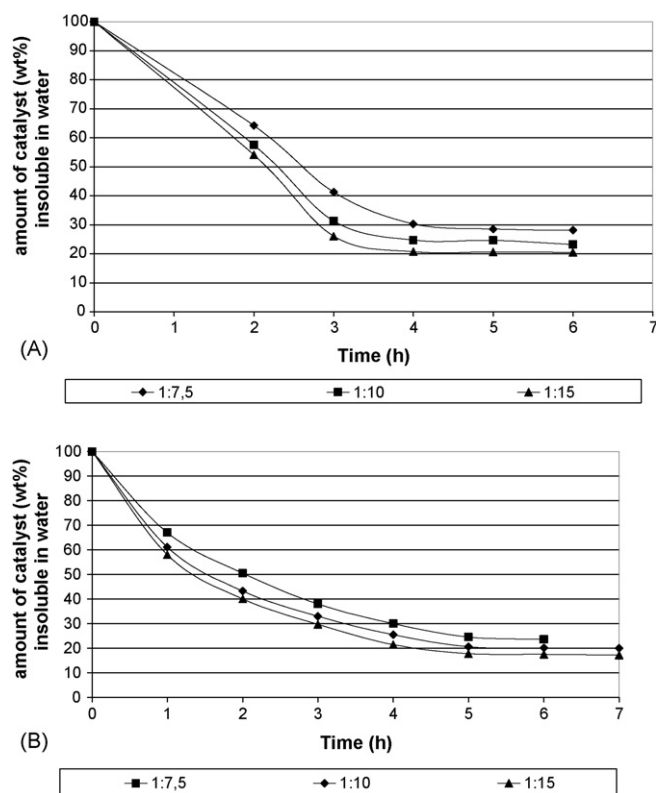

Fig. 2. Effect of the catalyst/flux mass ration on fusion process with KHSO$_4$ of the CoMo (A) and NiMo (B) catalysts at 350 °C.

the sample/flux mass ratio also increases as less flux is necessary to treat the sample.

3.3. Effect of temperature

One of the great challenges of pyrometallurgical processes is to save energy. They are generally employed only when there are no other alternatives for processing a spent material [21,22] under mild experimental conditions, which is the tendency observed in the recent literature [20].

One of the advantages of the acid fusion process over the common alkaline fusions [23,24] is its lower processing temperature. Alkaline fusions require temperatures over 500 °C (NaOH) or 850 °C (Na_2CO_3) for their effectiveness. In this study fusion with $KHSO_4$ was conducted in the range of 350–600 °C, using a catalyst/flux mass ratio of 1:10. The results are presented in Fig. 3.

The fusion at 350 °C presented a peculiar behavior when compared to the experiments carried out at higher temperatures. In this case the major portion of coke (only the volatile fraction was eliminated) remained in the insoluble residue since it is not reactive towards the flux. This explains why the amount of insoluble matter in water, after fusion at 350 °C, is 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 fusion of both samples, in the temperature range of 500–600 °C, reduced the time in 3 h when compared to the experiments carried out at 350 °C, taking, for both catalysts, around
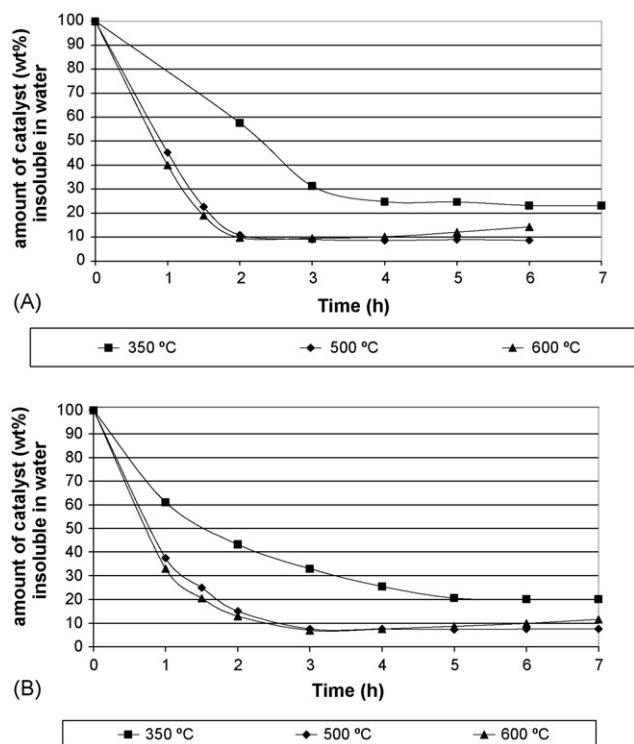
(A)

Legend: —■— 350 °C   —◆— 500 °C   —▲— 600 °C

(B)

Legend: —■— 350 °C   —◆— 500 °C   —▲— 600 °C

Fig. 3. Effect of temperature on the fusion of CoMo (A) and NiMo (B) catalysts with $KHSO_4$ (catalyst/flux mass ratio 1:10).

Table 2
Amount (wt.%) of coke present in the insoluble residue after fusion at 350 °C for 5 h

Catalyst	C (wt.%)
CoMo	40.7 ± 0.9
NiMo	59.9 ± 0.6

2–3 h. However, different behaviors were observed above 3 h. The amount of insoluble matter in water, after running the fusion process, in the experiments at 500 °C, remained the same with time but there was a clear trend to increase such amount when fusion is performed at 600 °C, thus suggesting the occurrence of reactions that form insoluble compounds. It is important to observe that the use of slow heating rates (4 °C min^{-1}) aimed at avoiding ignition of coke (*burn off*) thus forming overheating zones on the catalyst bed. Therefore it is believed that the additional insoluble residue, formed at 600 °C, for over 3 h, is unavoidably due to the formation of refractory compounds such as spinels (XAl_2O_4), phosphomolybdates, aluminosilicates and meta-silicates ($XSiO_3$) [20,25].

It is clear that working at 500 °C presents several advantages (lower energy consumption, lower losses of elements by formation of insoluble residues). However, an additional discussion is necessary to understand the behavior of the 350–500 °C temperature range.

The insoluble residue after fusion at 350 °C for 5 h was roasted in a furnace at 600 °C for 3 h. The solid obtained was cooled down in desiccators and weighed. The objective was to estimate the amount (wt.%) of coke in the original residue. After coke removal the solid exhibited a greenish (NiMo) or blue (CoMo) color. The data are presented in Table 2.

When the amount of carbonaceous deposits is subtracted from the overall insoluble residue, the catalysts presented different behaviors:

(a) CoMo catalyst: after elimination of coke the amount of insoluble matter decreased from 22.5 to 12.4 wt.%. This result is higher than the insoluble matter found after fusion of the same sample at 500 °C for at least 2 h (around 9.5 wt.%). This strongly suggests that coke presents a physical effect on fusion behavior at low temperatures, *i.e.*, it presents a covering effect on the reactive portion of the sample. The final result is the yield loss when compared to higher temperatures;

(b) NiMo catalyst: the amount of insoluble residue was reduced from 20.0 wt.% to about 8.2 wt.%. This result is very close to the amount of insoluble matter found after fusion at 500 °C (8.5 wt.%). Coke apparently did not present the same behavior as observed for the CoMo catalyst.

It must be emphasized that data for coke elimination refer to the insoluble residue after fusion at 350 °C, not to the original catalyst. This is justified due to the amount of carbonaceous deposits in this residue for the NiMo catalyst is higher than for the CoMo sample (Table 3). However the amount of coke in the CoMo spent original catalyst is about 20 wt.% higher

Table 3
Amount (wt.%) of the elements present in the insoluble residue after fusion at 500 °C for at least 2 h with respect to the original composition of the spent catalyst

Sample	Ni/Co	Mo	Al	P	Si
NiMo	5.0	<0.5	3.0	72	–[a]
CoMo	8.5	1.5	4.5	88	100

[a] Present in tiny amount in the spent sample.

(Table 1). The difference must be attributed to the amount of volatile organic matter on each case [26]. The original samples were roasted at 350 °C for 5 h. The amount of residual C obtained (Leco analyser) indicates that it corresponds to 92 wt.% of the original amount in the NiMo sample and 78 wt.% for the CoMo sample. Therefore, the last one contains more coke but it is also more volatile. On the other hand the original spent NiMo catalyst presents a higher surface area and also a higher pore volume (Table 1) than the CoMo catalyst. After roasting at 350 °C, the NiMo catalyst still presented higher surface area (112 m^2 g^{-1}) and pore volume (0.071 mL g^{-1}) than the roasted CoMo sample (respectively, 98 m^2 g^{-1} and 0.060 mL g^{-1}). Therefore, fusion at low temperatures in the presence of coke is a delicate balance between porosity and volatility of coke and the surface area of the spent sample.

Once described the effect of coke the next step was to investigate the inorganic matter in the insoluble residue after fusion. X-ray diffraction analyses were applied only to samples treated at 500 or 600 °C; coke present in the residue of fusions accomplished at 350 °C did not allow obtaining a diffractogram. The elimination of the residual coke could alter the crystallinity and the true inorganic phases present. Fig. 4 shows the diffractogram of the insoluble residue of the NiMo catalyst treated at 500 °C. It is a very poor crystallized solid but it is suggested the presence of the NiAl$_2$O$_4$ spinel.

Fig. 5 presents the X-ray diffractogram of the insoluble residue of the CoMo catalyst treated at 500 °C for 4 h. The crystallinity is higher and two phases were identified: cobalt meta-silicate (CoSiO$_3$), in agreement with the presence of silicon in this sample, and an aluminum–silicon oxide.

X-ray diffractograms of the insoluble residue obtained after fusion at 500 or 600 °C for more than 4 h presented the same features as above mentioned.
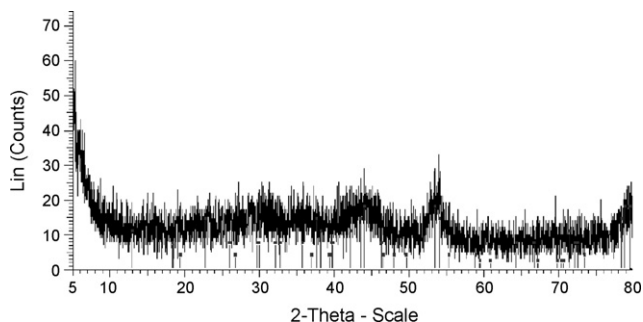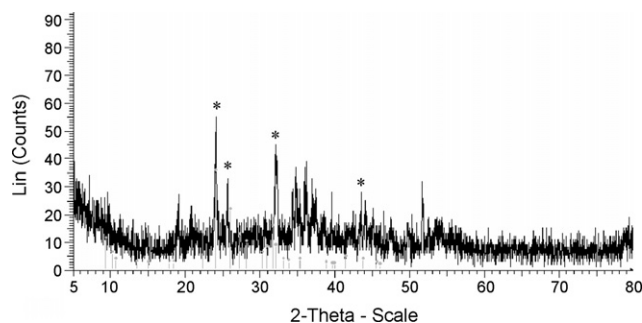

Fig. 5. X-ray diffractogram of the insoluble residue of the CoMo catalyst after fusion with KHSO$_4$ at 500 °C for 4 h: non-assigned peaks: cobalt meta-silicate (CoSiO$_3$); peaks assigned with an *: aluminum–silicon oxide.

The presence of CoSiO$_3$ and NiAl$_2$O$_4$ in the insoluble matter is relevant since such compounds reduce cobalt and nickel recoveries; this fact may also explain why recovery yields of those elements from the catalysts under study, in hydrometallurgical processes described in literature under mild experimental conditions, do not generally reach the theoretical yield of 100 wt.% [27,28].

The chemical analyses of the insoluble residue (dissolved in HF + HCl 1:1 v/v) are presented in Table 3. The most important losses (on a percentage basis) are for cobalt and nickel, whereas losses of molybdenum were very low or even negligible. All silicon and most phosphorus (as phosphate species) present in samples and some aluminum are the basic components of the insoluble residue, as refractory compounds that are not reactive with KHSO$_4$ under fusion.

3.4. Metals recovery

3.4.1. Recovery of cobalt and nickel

The overall processing scheme is shown in Fig. 6. The first step is the selective precipitation of nickel (or cobalt) by slow addition (dropwise) to the leachate of NaOH (6 mol L^{-1}) at room temperature with constant stirring (200 rpm). The pH must be kept at 12 or higher in order to keep aluminum and molybdenum solubilized as [Al(OH)$_4$]$^-$ and MoO$_4$$^{2-}$, respectively. The following reactions occur:

$$X^{2+} + 2NaOH \rightarrow X(OH)_2 + 2Na^{+,}$$

$$3X^{2+} + 2PO_4^{3-} \rightarrow X_3(PO_4)_2 \downarrow \quad (X = Ni, Co)$$
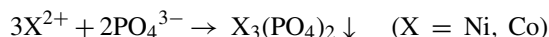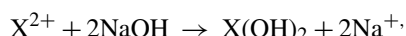
The precipitate was filtered and washed with water (4 mL g^{-1} of solid). The filtrate was colorless and presented no turbidity. The precipitated amount of each element depends on the relative amounts of solubilized nickel (cobalt) and phosphorous. Since most phosphorus remained in the insoluble residue (Table 3), the soluble phosphorus precipitated with nickel or cobalt and the excess of those metals as hydroxide.

3.4.2. Recovery of aluminum

Sulfuric acid (6 mol L^{-1}) was added to the colorless solution at room temperature under stirring (200 rpm). The final pH was in the range of 7–8, and aluminum precipitated as Al(OH)$_3$. Such precipitate was filtered and washed with NH$_4$OH 0.01 mol L^{-1}
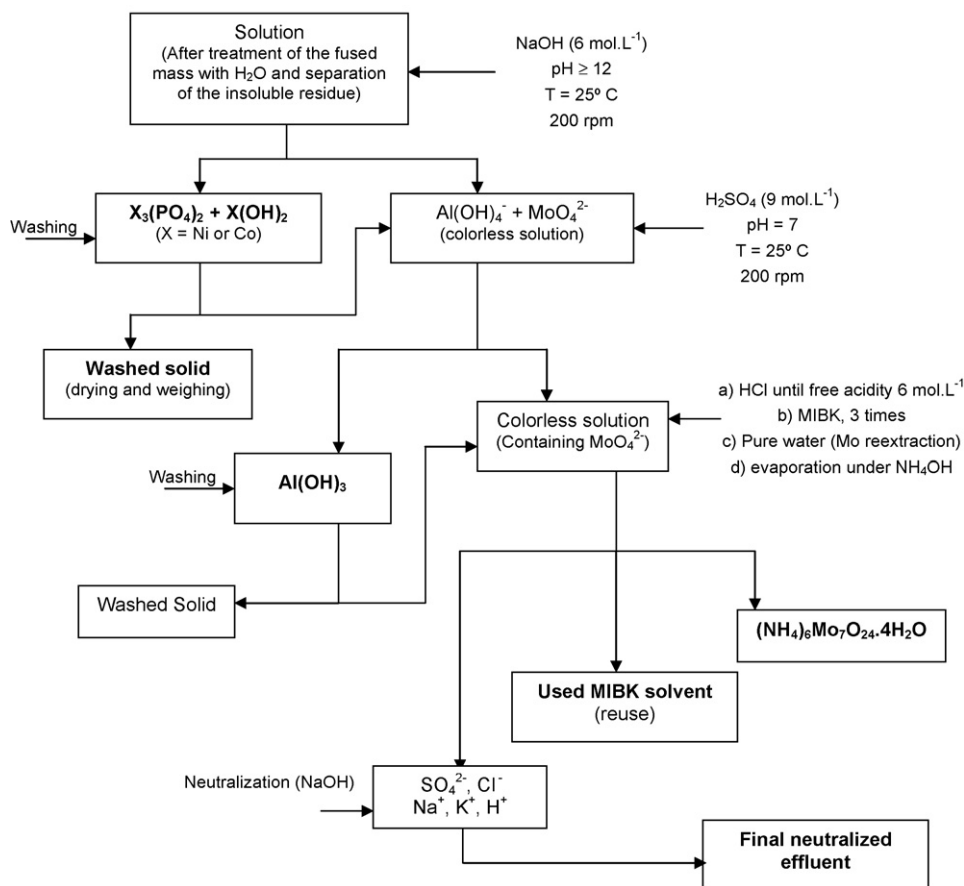

Fig. 4. X-ray diffractogram of the insoluble residue of the NiMo catalyst treated with KHSO$_4$ at 500 °C for 4 h.

Fig. 6. General scheme for recovery of Al, Ni (or Co) and Mo after catalyst fusion with $KHSO_4$ and dissolution of the fused mass in water.

$(10 \, mL \, g^{-1})$ and water $(4 \, mL \, g^{-1})$, in order to eliminate sulfate ions (test with $BaCl_2$ $(1 \, mol \, L^{-1})$ until absence of $BaSO_4$ precipitation). The solid was dried at $150 \, °C$ for $3 \, h$, cooled down in a desiccator and weighed.

3.4.3. Recovery of molybdenum

The absence of soluble phosphorus was essential for recovering molybdenum with high yields by solvent extraction with methyl-isobutylketone (MIBK). This extraction occurs in HCl solution [29], where significant losses of Mo as phosphomolybdate, $[(PMo_{12}O_{40})^{3-}]$, occurs. The neutralized solution, after aluminum recovery, was treated with concentrated HCl so that the free acidity was adjusted to $6 \, mol \, L^{-1}$. This solution was treated with the same volume of MIBK three times. The organic extracts were combined and treated with pure distilled water to recover molybdenum to the aqueous phase. This solution was evaporated under concentrated ammonium hydroxide, thus crystallizing ammonium heptamolybdate, $(NH_4)_7Mo_6O_{24}\cdot 4H_2O$, a white solid. During this procedure the gaseous effluent was washed down with distilled water at room temperature. Concentration of ammonium hydroxide can reach $10 \, mol \, L^{-1}$, which is suitable for crystallization of ammonium heptamolybdate. The used organic solvent can be used four times without significant decrease in molybdenum recovery.

The recovery yields are shown in Table 4. Mo and Al recoveries were very high. Co and Ni recoveries depended on the

losses in the insoluble residue after fusion, particularly at $350 \, °C$. However the recoveries shown in Table 4 are comparable or even surpass those normally cited in the pyro/hydrometallurgical processes reported in the literature [27,30], but under less drastic experimental conditions.

3.5. Final wastes management

The final aqueous acid solution after molybdenum extraction with MIBK was neutralized with NaOH $(6 \, mol \, L^{-1})$, giving a colorless solution (with no precipitate) of sodium/potassium sulfates/chlorides. The amounts of aluminum and molybdenum are below the detections limits established for atomic absorption spectrometry (Al, $0.5 \, mg \, L^{-1}$; Mo, $0.1 \, mg \, L^{-1}$). One gram of spent catalyst generated about $90 \, mL$ of final neutralized effluent. The other waste generated after fusion is the water insoluble matter. This residue can be sent to industrial dumps or co-processed [31–33] as mineralizing agent.

One of the most important aspects of a new recycling process is that the final wastes generated do not cause negative environmental impacts, making inviable the application of the process in a commercial scale. The greatest challenge of fusion with potassium hydrogen sulfate is to treat the gaseous effluent, which may contain very aggressive compounds such as SO_x. Under the best experimental conditions ($500 \, °C$, $2–3 \, h$, catalyst/flux mass ratio $1:10 \, wt.\%$) the amount of $BaSO_4$ precipitated indicates

Table 4
Recovery yields of Ni, Co, Mo and Al present in NiMo and CoMo spent catalysts treated with fusion with $KHSO_4$ at 350 and 500 °C, according to the general processing scheme presented in Fig. 6

Catalyst	Product	Metals recovered (wt.%)			Temperature (°C)
		Ni or Co	Mo	Al	
CoMo	$Co_3(PO_4)_2 + Co(OH)_2$ (blue precipitate)	87.6 ± 0.2	Not detected	Not detected	350
		90.9 ± 0.5	Not detected	Not detected	500
NiMo	$Ni_3(PO_4)_2 + Ni(OH)_2$ (green precipitate)	91.6 ± 0.4	< 0.05	Not detected	350
		94.2 ± 0.8	Not detected	Not detected	500
CoMo	$Al(OH)_3$ (white solid)	0.05 ± 0.01	Not detected	94.5 ± 1.1	350
		Not detected	Not detected	95.6 ± 0.7	500
NiMo		0.05 ± 0.01	Not detected	90.2 ± 0.9	350
		Not detected	Not detected	92.8 ± 0.7	500
CoMo	$(NH_4)_7Mo_6O_{24}\cdot 4H_2O$ (white solid)	Not detected	96.2 ± 0.5	Not detected	350
		Not detected	99.2 ± 0.2	0.05	500
CoMo		Not detected	95.9 ± 0.6	<0.05	350
		Not detected	97.4 ± 0.5	not detected	500

that about 10 wt.% of the excess of flux employed decomposed ($2KHSO_4 \rightarrow K_2S_2O_7$ ($+H_2O$) $\rightarrow K_2SO_4 + SO_3$), giving SO_3. This means that each gram of the spent catalyst processed will generate about 0.15 g of the trioxide. SO_2 and H_2S were not detected in the gaseous effluent, since an oxidizing atmosphere was kept in the furnace during fusion (Section 2.2). The above result agrees reasonably well with literature data [34]. The best way to treat the (acid) waste is to add a strong base (such as NaOH), giving a neutral solution of Na_2SO_4.

4. Conclusions

The fusion of spent HDR catalysts with $KHSO_4$ allowed a good overall metals recovery. The process itself required less drastic experimental conditions when compared to the classical pyro/hydrometallurgical processes. It is not necessary to use more than the double of the stoichiometric amount of flux to accomplish the fusion under a reasonable time. The presence of phosphorus and sulfur did not influence significantly the fusion process and the metals recovery step. Silicon compounds were not reactive under fusion, thus reducing the amount of cobalt or nickel that can be recovered this way. This fact represents the limitation of the acid fusion, i.e., the applicability is limited to the catalyst support that reacts with the flux (basic or amphoteric oxides).

Temperature is a very critical parameter. The fusion at 350 °C lead to loss of yield due to the presence of residual coke (occlusion of the catalyst surface), whereas the fusion at 500 °C or higher temperatures eliminated all carbonaceous matter and reduced the time of fusion but presented the risk of formation of refractory compounds (spinels, silicates, etc.) which reduced considerably the metals recovery yield. It seems to exist an optimum temperature range (450–500 °C) where the insoluble matter after fusion reaches a minimum amount.

Another advantage of the acid fusion process is the generation of low amounts of final wastes, which present low toxicity. The solid waste can be co-processed and the final (neutralized) effluent is a solution of alkali chlorides/sulfates. This situation is simpler than the scenario found for many proposed recovery processes mentioned in the literature. For example, the use of the toxic sulfide to precipitate Ni, Co and Mo is avoided, being replaced by direct precipitation (Ni/Co) or solvent extraction techniques (Mo).

References

[1] J.N. Armore, New catalytic technology commercialized in the USA during the 1990s, Appl. Catal. A 222 (2001) 407–426.
[2] B.B. Kar, B.V.R. Murthy, V.N. Misra, Extraction of molybdenum from spent catalyst by salt-roasting, Int. J. Miner. Proc. 76 (2005) 143–147.
[3] Background document: clarifying the scope of petroleum hazardous waste listings: supplemental information regarding petroleum hydroprocessing units, The US Environmental Protection Agency, Office of Solid Waste, Washington, USA, 2002, p. 55.
[4] M. Marafi, A. Stanislaus, Options and processes for spent catalyst handling and utilization, J. Hazard. Mater. 101 (2003) 123–132.
[5] K. Okabe, Results in reduction of environmental impact, Cosmo Oil Environmental Report 2001, Tokyo, Japan, 2001, pp. 15–16.
[6] Waste management procedures, Oklahoma Medical Research Foundation, Oklahoma City, US, 2002, (http://www.omrf.org/OMRF/Safety/SafetyManual/WMP.pdf).
[7] Environmental Protection Agency—Ignitable and Combustible wastes K171 and K 172, Federal Register 68 (2003) 59940–59941.
[8] Catalog of Hazardous and Solid Waste Publications, The US Environmental Protection Agency, Office of Solid Waste, Washington, US, 2003, p. 116.
[9] Petroleum Refining Listing Determination Proposed Rule Response to Comment Document. Part II, The US Environmental Protection Agency, Office of Solid Waste, Washington, USA, 1998, p. 69.
[10] Wastes co-processing, Directory No 264 from the National Brazilian Environmental Council, Federal Official Journal, March 20, 2000, (http://www.mma.gov.br/port/conama).
[11] I. Wernick, N.J. Themelis, Recycling metals for the environment, Annu. Rev. Energy Environ. 23 (1998) 465–477.
[12] Petroleum Refining Process Waste Listing Determination—Supplemental Background Document: Groundwater Pathway Risk Analysis, The US

Environmental Protection Agency, Office of Solid Waste, Washington, US, 1997, p. 65.

[13] Y. Chen, Q. Feng, Y. Shao, G. Zhang, L. Ou, Y. Lu, Research on the recycling of valuable metals in spent Al_2O_3-based catalyst, Miner. Eng. 19 (2006) 94–97.

[14] D. Santhiya, Y.P. Ting, Bioleaching of spent refinery processing catalyst using *Aspergillus niger* with high-yield oxalic acid, J. Biotechnol. 116 (2005) 171–184.

[15] D. Santhiya, Y.P. Ting, Use of adapted *Aspergillus niger* in the bioleaching of spent refinery processing catalyst, J. Biotechnol. 121 (2006) 62–74.

[16] W. Mulak, B. Miazga, A. Szymczycha, Kinetics of nickel leaching from spent catalyst in sulphuric acid solution, Int. J. Miner. Proc. 77 (2005) 231–235.

[17] P.C. Campos, T.S. Lima, J.C. Afonso, Metals recovery from spent hydrotreatment catalysts in a fluoride-bearing medium, Hydrometallurgy 80 (2005) 211–219.

[18] L. Luo, T. Miyazaki, A. Shibayama, W. Yen, E. Fujita, A novel process for recovery of tungsten and vanadium from a leach solution of tungsten alloy scrap, Miner. Eng. 16 (2003) 665–670.

[19] Environmental Protection Agency—hazardous waste management system: identification and listing of hazardous waste, final rule and proposed rule, Federal Register 63 (1998) 42110–42189.

[20] A.B. Luz, Zeólitas: Propriedades e Usos Industriais, Série Tecnologia Mineral No 55, CETEM/CNPq, Rio de Janeiro, 1995.

[21] N.I. Gerhardt, A.A. Palant, V.A. Petrova, R.K. Tagirov, Solvent extraction of molybdenum (VI), tungsten (VI) and rhenium (VII) by diisododecylamine from leach liquors, Hydrometallurgy 60 (2001) 1–5.

[22] P. Zhang, K. Inoue, H. Tsuyama, Recovery of cobalt and nickel from spent hydrodesulfurization catalysts by liquid–liquid extraction, Kagaku Kogaku Ronbunshu 21 (1995) 457–464.

[23] B.B. Kar, P. Datta, V.N. Misra, Spent catalyst: secondary source for molybdenum recovery, Hydrometallurgy 72 (2004) 87–92.

[24] F. Delmas, C. Nogueira, I. Dalrymple, J. Parkes, Metals recovery from hydrodesulfurization catalysts, in: Hydrometallurgy '94 Pop. International Symposium, Chapman and Hall, London, UK, 1994, pp. 1075–1086.

[25] R.K. Clifford, Spent Catalyst Management Petroleum Technology Quarterly, Crambeth Allen Publishing, Shropshire, Spring, 1997, pp. 33–39.

[26] R. Huges, Catalyst Deactivation, Academic Press, London, 1984.

[27] A.A. Palant, N.A. Iatsenko, V.A. Petrova, Solvent extraction of molybdenum (VI) by diisododecylamine from sulphuric acid solution, Hydrometallurgy 48 (1998) 83–90.

[28] J. Marchese, F. Valenzuela, C. Basualto, A. Acosta, Transport of molybdenum with Alamine 336 using supported liquid membrane, Hydrometallurgy 72 (2004) 309–317.

[29] G.R. Waterbury, C.E. Bricker, Separation and determination of microgram amounts of molybdenum, Anal. Chem. 29 (1957) 129–135.

[30] E. Furimsky, F.E. Massoth, Deactivation of hydroprocessing catalysts, Catal. Today 52 (1999) 381–495.

[31] J. Payá, J. Monzó, M.V. Borrachero, S. Velásquez, Evaluation of the pozzolanic activity of fluid catalytic cracking catalyst residue (FC3R). Thermogravimetric analysis studies on FC3R-Portland cement pastes, Cement Concrete Res. 33 (2003) 603–609.

[32] N. Su, Z.H. Chen, H.Y. Fang, Reuse of spent catalyst as fine aggregate in cement mortar, Cement Concrete Compos. 23 (2001) 111–118.

[33] M. Bukowska, B. Pacewska, I. Wilinska, Influence of spent catalyst used for catalytic cracking in a fluidized bed on sulphate corrosion of cement mortars. I. Na_2SO_4 medium, Cement Concrete Res. 34 (2004) 759–767.

[34] I.A. Piskunova, A.A. Lysenko, O.V. Astashkina, M.O. Basok, Derivatographic studies of the thermal behavior of some salts, Fibre Chem. 35 (2003) 168–171.