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THE IMPORTANCE OF PRE-TREATMENT OF SPENT HYDROTREATING CATALYSTS ON METALS RECOVERY

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This work describes a three-step pre-treatment route for processing spent commercial NiMo/Al_2O_3 catalysts. Extraction of soluble coke with n-hexane and/or leaching of foulant elements with oxalic acid were performed before burning insoluble coke under air. Oxidized catalysts were leached with 9 mol L^{-1} sulfuric acid. Iron was the only foulant element partially leached by oxalic acid. The amount of insoluble matter in sulfuric acid was drastically reduced when iron and/or soluble coke were previously removed. Losses of active phase metals (Ni, Mo) during leaching with oxalic acid were compensated by the increase of their recovery in the sulfuric acid leachate.

Keywords: spent catalyst; metals recovery; foulant elements.

INTRODUCTION

The amount of metal-fouled spent catalysts from hydroprocessing units has increased significantly worldwide in recent years due to a rapid growth of the residual and heavy oil upgrading capacity by hydroprocessing.[1,2] The goal is to meet the increasing demand for ultra-low sulfur fuels.[3] These feedstocks contain considerable amounts of sulfur, nitrogen and metals. NiMo and CoMo/Al_2O_3 are typical examples of spent catalysts coming from hydrotreating (HDT) units.[4-6] The lifetime of the catalysts tends to decrease due to the more severe operations required.[3,4,7] Catalyst deactivation is basically due to coke and metals deposition over its surface. This phenomenon is characterized by a considerable loss of surface area and especially by a dramatic decrease of the catalytic activity.[2,8,9]

Disposal of spent catalyst requires compliance with stringent environmental regulations. They are basically regarded as solid waste.[10] Spent HDT catalysts have been classified as dangerous wastes by the "United States Environmental Protection Agency" (USEPA).[1-5] They may release toxic gases, are subject to spontaneous ignition and present heavy metals and carcinogenic compounds. Even after calcination at high temperature metals such as nickel, vanadium, cobalt and molybdenum may be leached with water.[11] The amounts leached may surpass the limits established by the protocol Nº. 3987 from the "American Society for Testing Materials" (TCLP – "toxic characteristic leaching procedure"). There are many strategies to manage the spent catalyst: regeneration, rejuvenation, co-processing and metals recovery (recycling). The choice depends on technical and economical viability.[4] Particularly many researches have been performed to process spent non-regenerable samples, because there is a limited number of regeneration cycles.[3] A slow but irreversible degradation of the catalyst structure takes place after each cycle.[2]

In some cases it is possible to restore much of the original catalytic activity by removing the deactivation agent and/or reversing its effects on the active phase.[1,12] This is only possible when deactivation is reversible (as coke fouling). Coke removal via oxidation is a delicate task and requires a careful temperature control. The reaction is highly exothermic and can easily result in overheating and in thermal reorganization of the sample. The final result is the loss of surface area (sintering) and the formation of refractory compounds.

Many contaminants may be found in spent HDT catalysts. They may come from the feedstocks (V, Ni, Ca, As, Fe, Na), additives in some refining processes (Si), or corrosion (Fe).[13] Poisoning of active sites by elements such as S, V and As, and sintering are basically irreversible. Depending on the process it is not advisable to regenerate a spent catalyst containing more than 1-3 wt.% V and 0.2-0.4 wt.% As.[13] Elements such as Na and Si do not allow full activity recovery after regeneration.[13] V destroys the mechanical strength of the alumina support pellets.[9] Even after coke removal some V and Ni remain in the treated catalyst. They act as a diffusion barrier for the reactants.[1,14] Fe acts as a physical blocker of active sites.[13]

Foulant elements may be at least partially removed by chemical leaching. The main challenge is to remove them elements without removing those of the active phase and catalyst support. Generally the concentration of the leachant is relatively low (< 1 mol L^{-1}), whereas the foulant elements (Fe, V, Ni, Ca etc.) correspond up to 15 wt.% of the spent catalyst.[1,9,15] Some studies employ leaching with inorganic acids. For instance, 0.1 mol L^{-1} HCl leached 87 wt.% Ca and 37 wt.% Fe from a spent NiMo/Al_2O_3 catalyst after 24 h at 25 °C.[9] Most researches employ chelating agents.[10] Leaching is influenced by parameters such as temperature, chelating agent concentration, time, stirring and pH.[14,15] An optimal chelating agent should display high leaching efficiency, a high selectivity for the foulant element, a high solubility and a high thermodynamic stability of the formed complex.[14,16] Oxalic acid has been one of the chelating agents most employed. Ammonium oxalate and mixtures of ammonium hydroxide and ammonium oxalate have also been employed.[7,14,17-19] There are relatively few studies on the effect of soluble coke in organic solvents and leaching of foulant elements on metals recovery from spent catalysts. This is in contrast to the studies on their effect on catalyst regeneration/rejuvenation.[1,7,14,17] The key question is to understand the role of soluble coke and foulant elements on metals recovery after the controlled burning of insoluble coke.

This work aims at describing the influence of previous removal of soluble coke and foulant elements before insoluble coke burning on metals recovery from spent HDT catalysts. The goal was to increase

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solubility of catalyst components (particularly those of the active phase) via leaching with sulfuric acid, following a procedure established in our group.[6] The spent original catalyst was used as reference. The effectiveness of both pre-treatments was assessed by the amount and composition of insoluble matter after leaching with sulfuric acid.

EXPERIMENTAL

Samples

Two spent commercial NiMo/Al_2O_3 catalysts were used in this study. They were kept in their original form (5 mm cylinder extruded, 1.2 mm diameter). These catalysts were employed in the period 2004-2008 in diesel/heavy oil hydrotreaters in Brazilian refineries. X-ray fluorescence (XRF) analysis showed the presence of three foulant elements: iron, calcium and arsenic (they are absent in the fresh catalysts[6,11,18]). Silicon and phosphorous are support additives of both catalysts.[6,11,18] Chemical compositions are given in Table 1. The active phase of the catalysts was sulfided during their lifetime in the hydrotreater unit. The contact with air during storage (or catalyst handling) may lead to the partial oxidation of sulfides.

Table 1. Chemical analysis (wt.%, dry basis) of spent NiMo/Al_2O_3 catalysts

Component		average wt.%	
		NiMo 1	NiMo 2
Support	Al_2O_3	45.3	48.2
*Active phase**	MoO_3	9.7	9.2
	NiO	2.5	2.0
	SO_3	25.7	23.8
Support additives	SiO_2	5.0	2.3
	P_2O_5	2.6	2.2
*Foulant elements***	Fe_2O_3	1.6	1.6
	CaO	0.2	0.6
	As_2O_3	0.1	0.4
	C (coke)	7.4	9.5

* the active phase is composed by mixed nickel and molybdenum sulfides (NiMoS)[7] ** elements already present in the feedstocks (Fe, Ca, As), formed by lines corrosion (Fe) or during feedstock HDT[13]

Extraction of soluble coke

50 g of the original spent catalyst (or the one previously leached with oxalic acid (see below) were introduced into a soxhlet apparatus and treated with n-hexane for 6 h under reflux, in order to extract the soluble coke. After this procedure, the solvent was removed under vacuum. The organic matter recovered was weighed.

Leaching of foulant elements

50 mL of aqueous oxalic acid was put into contact with 5 g of the sample (solid/liquid ratio = 1/10 g mL^{-1}). This sample can be the original spent catalyst or the one treated with n-hexane (see above). The following experimental parameters were varied: i) temperature (25-75 ºC); ii) time (30-90 min); iii) oxalic acid concentration (0.04-0.12 mol L^{-1}). Stirring was fixed at 200 rpm. An excessive stirring tends to break catalyst extrudates, exposing the support and the active phase to the leachant. A slow stirring decreases leaching yield.[10,14] After the experiments the leached catalysts were filtered of, washed with water, dried at 150 ºC for 2 h, cooled down in a dessicator and weighed. The reproducibility of leaching was determined to be on the order of ± 3%, by repeating the experiments thrice.

In another set of experiments, model compounds were submitted to the leaching procedure applied to catalyst samples. FeS, NiS and MoS_2 were prepared according to procedure described in the literature.[20] $CaCl_2$, As_2O_3, CaO, $Ca(AsO_2)_2$, SiO_2, $NiSO_4$, $Fe_2(SO_4)_3$ and MoO_3 were supplied by Merck and were used as received. The mass of each compound cited above employed in the experiments contains the same amount of the element present in the 5g of the catalyst sample.

Removal of insoluble coke

All the samples (the original spent catalysts, the ones treated with n-hexane + oxalic acid, oxalic acid + n-hexane, oxalic acid only and n-hexane only) were placed in crucibles and introduced in a furnace. The insoluble coke was burned under the following conditions: heating rate, 1 ºC min^{-1}; final temperature, 500 ºC; time, 4 h. The oxidized samples were cooled down in the furnace and transferred to a dessicator. The sample mass before and after coke burning was determined in order to evaluate the amount of volatiles (carbon, moisture and sulfur) eliminated during this step.

Leaching of pre-oxidized catalysts

These experiments were carried out using 9 mol L^{-1} sulfuric acid following the experimental procedure described elsewhere.[6] The catalyst/leachant ratio was 1/10 (g mL^{-1}). The insoluble matter was filtered of, washed with water (4 mL g^{-1}), dried at 110 ºC for 2 h and weighed. Leaching was run in triplicate, and errors for each experiment were always below 2%. Some model compounds were leached under the above conditions: $Ni_3(PO_4)_2$, $NiSiO_3$ and $NiMoO_4$ were prepared by reaction between $NiSO_4$ and Na_3PO_4, Na_2SiO_3 or Na_2MoO_4. These compounds were calcined at 500 °C for 4 h prior to the experiments.

Analytical methods

Metals were analyzed by X-ray fluorescence (solids) or atomic absorption spectrometry (solutions). Metals in the leachates were also investigated by classical qualitative analysis.[21,22] pH of leachates was measured with a digital pH meter. Textural properties of the spent and pre-treated catalysts (pore volume and surface area) were determined by the BET method (N_2 adsorption/desorption at -196 °C). Sulfate ions were determined by ion-chromatography.

RESULTS AND DISCUSSION

Removal of soluble coke

About 3 wt.% of the total carbonaceous deposits (0.2-0.3 wt% of the spent catalyst) was dissolved in n-hexane in both samples. This result agrees with literature data.[23-26] The main feature of this organic matter is its high reactivity towards oxidation as seen in temperature-programmed oxidation experiments.[23,25,26] Soluble coke contains more hydrogen than the insoluble one. As usual, solvents are not effective in removing insoluble coke.[2,17,19]

Effect of experimental parameters on leaching with oxalic acid

The influence of the oxalic acid concentration is presented in Table 2. A net increase on iron leaching was observed when concentration was doubled (0.04-0.08 mol L^{-1}). This effect was less pronounced for Ni, Mo and S. Concentrations above 0.08 mol L^{-1}

did not change significantly elements leaching. P, Si, Ca and As were not leached. Other studies show that there is a leachant concentration above which the effect on leaching is negligible: 0.33 mol L^{-1} or 0.66 mol L^{-1} oxalic acid;[1,15] 0.5 mol L^{-1} HCl.[9] The amount of foulant elements and coke (Table 1) are lower in the samples under study than in the catalysts reported in the literature. This fact explains the low optimum oxalic acid concentration (0.08 mol L^{-1}) found in this work.

Table 2. Effect of oxalic acid concentration on leaching spent NiMo/Al_2O_3 catalysts (25 ºC, 200 rpm, 30 min)

Component	wt.% leached $H_2C_2O_4$ 0.04 mol L^{-1}		wt.% leached $H_2C_2O_4$ 0.08 mol L^{-1}		wt.% leached $H_2C_2O_4$ 0.12 mol L^{-1}	
	NiMo 1	NiMo 2	NiMo 1	NiMo 2	NiMo 1	NiMo 2
Support						
Al_2O_3	< 0.1	0.1	0.1	0.1	0.1	0.2
Active phase						
MoO_3	0.1	< 0.1	0.3	0.1	0.3	0.1
NiO	0.2	0.1	0.8	0.6	0.9	0.6
SO_3	1.5	1.2	1.7	1.5	1.7	1.5
Support additives						
SiO_2/P_2O_5	negligible		negligible		negligible	
Foulant elements						
Fe_2O_3	12	16	32	34	31	35
CaO/As_2O_3	negligible		negligible		negligible	

Results of the combined effect of temperature and time on leaching are presented in Table 3. Again, Fe is the only foulant element partially soluble in oxalic acid. Very small amounts of Ca and As were leached at 50 ºC. Leaching times longer than 60 min and temperatures above 50 ºC did not increase significantly solubilization of all elements. Leaching of active phase components was very low (< 1 wt.%). The influence of time on leaching depends on the amount of leachant and foulant elements.[1,9] In general, this procedure is performed at 50 ºC or lower temperatures.[1,9,10]

As a general rule, P, Si, Ca and As were not leached to a considerable extent. Addition of $CaCl_2$ containing the same amount of calcium present in the catalyst (5 g) to 50 mL of 0.08 mol L^{-1} oxalic acid at 25 or 50 ºC produced a white precipitate (CaC_2O_4). The K_{sp} of this salt was surpassed under our experimental conditions.[21,22] pH of the leachate was around 1.3, which was not sufficient to dissolve it.[22] $Ca(AsO_2)_2$, CaO and As_2O_3 were not affected by the leachant whatever the volume used and the temperature (25 or 50 ºC). The absence of complexing reactions between oxalate ions and Si or P makes their leaching negligible in all experiments.

Since the catalysts (their active phase) were sulfided during their lifetime in the hydrotreater unit, sulfur was originally present as sulfide species in the spent catalyst. Its solubility was low in all experiments. Addition of soluble Pb^{2+} to the leachates did not produce a brown precipitate (PbS), but a white one was formed ($PbSO_4$ + PbC_2O_4).[21,22] Addition of Ba^{2+} ions produced a white precipitate, which is partially soluble in hot concentrated HCl (BaC_2O_4), leaving a solid residue ($BaSO_4$). This indicates that soluble sulfur corresponds to sulfate species, and implies that some sulfide was oxidized during storage and catalyst handling.[9] For this reason, the relationship between leached Fe, Ni and Mo and soluble sulfur was investigated. Fe from the feedstock or corrosion[13] was converted to iron sulfide by H_2 and H_2S generated during HDT. The oxidation of sulfides can be described by the following reactions:

Table 3. Combined effect of temperature and time on leaching spent NiMo/Al_2O_3 catalysts with 0.08 mol L^{-1} oxalic acid (200 rpm)

Component	Time (min)	wt.% leached 25 ºC		wt.% leached 50 ºC		wt.% leached 75 ºC	
		NiMo 1	NiMo 2	NiMo 1	NiMo 2	NiMo 1	NiMo 2
Support							
Al_2O_3	30	0.2	0.2	0.7	0.6	0.7	0.7
	60-90	0.5	0.4	0.9	0.7	0.8	0.7
Active phase							
MoO_3	30	0.3	0.1	0.6	0.3	0.7	0.3
	60-90	0.4	0.1	0.7	0.4	0.7	0.4
NiO	30	0.8	0.6	0.9	0.6	0.9	0.7
	60-90	1.0	0.7	0.9	0.7	1.0	0.8
SO_3	30	1.7	1.5	2.4	2.0	2.6	2.1
	60-90	1.8	1.7	2.4	2.3	2.3	2.3
Additives							
SiO_2 and P_2O_5	30, 60 or 90	negligible		negligible		negligible	
Foulant elements							
Fe_2O_3	30	32	34	44	48	47	50
	60-90	35	37	47	50	49	49
CaO	30	negligible		0.1	0.2	0.3	0.5
	60-90	negligible		0.2	0.3	0.3	0.5
As_2O_3	30	negligible		< 0.1	0.1	0.2	0.3
	60-90	negligible		0.1	0.2	0.2	0.3

$$NiS + 2\,O_2 \rightarrow NiSO_4 \qquad (1)$$

$$2\,MoS_2 + 9\,O_2 + 2\,H_2O \rightarrow 2\,MoO_2SO_4 + 2\,H_2SO_4 \qquad (2)$$

$$2\,FeS + H_2SO_4 + 9/2\,O_2 \rightarrow Fe_2(SO_4)_3 + H_2O \qquad (3)$$

$$2\,FeS + H_2O + 9/2\,O_2 \rightarrow 2\,Fe(OH)SO_4 \qquad (4)$$

These reactions are highly exothermic, thus justifying one of the risks of the spent catalyst: their flammability (spontaneous combustion), according to the USEPA.[1,3-5] This explains why discharged spent HDT catalysts are stored under inert atmosphere (N_2).

On the basis of the metal content in Table 1 and the amount leached by oxalic acid (Table 3), it was searched for a correspondence between leached Fe, Ni and Mo and soluble S (as sulfate). From equations 2 to 4, oxidation of MoS_2 (1 MoO_3) gives two SO_4 units (2 SO_3). Oxidation of NiS (1 NiO) gives one SO_4 unit (1 SO_3). Conversion of two FeS (1 Fe_2O_3) produces two SO_4 units (2 SO_3). Table 4 presents the comparative data based on sulfur released (as sulfate) via oxidation of metal sulfides and soluble sulfur. The agreement is reasonable in all cases. The higher reactivity of FeS is explainable since it is deposited over the catalyst surface, being more susceptible to oxidation by exposure to air, whereas the active phase is covered by coke and other foulant species. Based on the amount of leached Ni, Fe and Mo (Table 3), addition of $NiSO_4$, $Fe_2(SO_4)_3$ or MoO_3 to 50 mL 0.08 mol L^{-1} oxalic acid at 25 or 50 ºC did not give any precipitate. Under pH of the leachate (1.3) Mo is predominantly present as MoO_2^{2+} species.[27]

Table 4. Correspondence between released S (as SO_4^{2-} ions) via oxidation of Fe, Ni and Mo sulfides and soluble sulfur (SO_4^{2-}). Leaching with 0.08 mol L^{-1} oxalic acid (200 rpm, 60 min), no soluble coke extraction

	25 ºC		50 ºC		75 ºC	
	NiMo 1	NiMo 2	NiMo 1	NiMo 2	NiMo 1	NiMo 2
Released S (mg)	21.0	19.3	28.6	27.4	29.6	27.0
Soluble S (mg)	23.1	20.2	30.8	27.3	28.9	27.3

The test with ammonium thiocyanate in the leachate gave a dark red color, thus confirming the presence of Fe(III). Fe^{2+} was not detected by the test with 1,10-phenanthroline.[21,22] Thus, when FeS reacts with oxygen, both elements are oxidized (Eq. 4 and 5).

Our data does not confirm a direct reaction between metal sulfides and oxalic acid, as stated in the literature.[1,15] For instance the reaction for FeS is:

$$FeS + 2\,H_2C_2O_4 \rightleftharpoons Fe(C_2O_4)_2^{2-} + 3\,H^+ + HS^- \qquad (5)$$

Under our experimental conditions FeS, NiS and MoS_2 were not significantly leached by 0.08 mol L^{-1} oxalic acid. Perhaps concentration of the chelating agent should be higher.[1,15] The low concentration of Fe(III), an oxidizing agent produced according to Eq. 4 and 5, could account for this fact.[1,4] Oxalic acid alone is less reactive towards sulfide leaching (in general, the metal is in the lowest oxidation state). In a separate experiment, 5.0 g of the spent catalysts were leached with 0.08 mol L^{-1} oxalic acid at 50 ºC for 60 min containing 0.08 mol L^{-1} $Fe(NO_3)_3$.[1] Fe leaching increased 50%, whereas Ni and Mo solubilities increased about six fold. Under these conditions NiS, MoS_2 and FeS were partially leached. Addition of Pb^{2+} did not produce a brown precipitate (PbS), whereas Fe^{2+} ions were not detected. Under low concentrations of oxalic acid it appears that leaching of foulant elements and active phase components of the spent catalyst is only feasible after oxidation of preexisting sulfides.

All oxidation products shown in Eq. 2-5 are water soluble. However, leaching with pure water at 50 ºC for 60 min gave lower yields (~30 wt.% Fe leached). The complexing character of oxalic acid (a chelating agent) improves metal leaching. This fact reflects that the mass transfer in the coke structure is the rate-controlling step.[1,9]

Even low leaching levels (1 wt.%) of the active phase components means losses of valuable metals.[6,10] Therefore, it is better to extract partially the foulant elements than to increase losses of catalyst components during leaching with oxalic acid. This reason also limits the concentration of the leachant in order to remove preferably the foulant elements rather than the catalyst components when the objective is to recover the active phase metals.

The influence of removal of soluble coke before metals leaching with oxalic acid

According to data on Table 5, previous removal of soluble coke increased somewhat metals leaching (Table 6) due to a slight increase of surface area and porosity of the catalyst.[1,9,10,15]

Although previous leaching with oxalic acid also increased somewhat the textural properties of the spent catalyst (Table 6), this procedure did not influence significantly the amount of soluble coke extracted by n-hexane after 6 h (3 wt.%). No organic matter in suspension was found in the leachate.

Table 5. Textural properties of the spent catalysts

Sample	Catalyst	BET surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})
Original	NiMo 1	137	0.24
	NiMo 2	141	0.27
Pre-extracted with n-hexane	NiMo 1	141	0.27
	NiMo 2	142	0.28
Pre-leached with oxalic acid	NiMo 1	140	0.26
	NiMo 2	143	0.30
Pre-extracted with n-hexane and pre-leached with oxalic acid	NiMo 1	145	0.28
	NiMo 2	146	0.30
Pre-leached with oxalic acid and pre-extracted with n-hexane	NiMo 1	145	0.29
	NiMo 2	145	0.31

Table 6. Effect of soluble coke removal on metals leaching with oxalic acid (0.08 mol L^{-1}, 200 rpm, 60 min, 50 ºC)

Component	wt.% leached no soluble coke extraction		wt.% leached previous soluble coke extraction	
	NiMo 1	NiMo 2	NiMo 1	NiMo 2
Support				
Al_2O_3	0.9	0.7	1.0	0.8
Active phase				
MoO_3	0.7	0.4	0.9	0.5
NiO	0.9	0.7	1.1	0.9
SO_3	2.4	2.3	2.6	2.6
Additives				
SiO_2 and P_2O_5	Negligible		Negligible	
Foulant elements				
Fe_2O_3	47	50	49	53
Cão	0.2	0.3	0.2	0.3
As_2O_3	0.1	0.2	0.1	0.2

Removal of insoluble coke

Coke was quantitatively removed from all samples. The volatile matter corresponds to 18 wt.% (NiMo 1) or 19.5 wt.% (NiMo 2) of the spent sample. The amount reported in the literature is generally higher (> 25 wt.%) basically because the amount of coke is lower in the samples under study.[6,10,18,19]

Previous leaching with oxalic acid did not change the release of volatiles. A similar result after leaching a spent NiMo catalyst with 0.1 mol L^{-1} HCl was found.[9] Previous soluble coke extraction slightly decreased the amount of volatiles: 17.7 (NiMo 1) and 19.1 wt.% (NiMo 2). Soluble coke corresponds to a small portion of the overall coke. These amounts were also found in the samples submitted to both pre-treatments, whatever the sequence.

Leaching with sulfuric acid

32 wt.% (NiMo 1) or 21 wt.% (NiMo 2) of the spent original sample was insoluble in sulfuric acid under our experimental conditions (Table 7). As expected, the main elements present in the solid residue are Si (fully insoluble), P and Al. However, more than 10 wt.% Mo was lost as insoluble compounds.

Samples submitted to at least one treatment before coke burning showed a significant decrease of the amount of insoluble matter

Table 7. Amount of insoluble components in 9 mol L^{-1} sulfuric acid (80 ºC, 200 rpm, 2h)

Component	wt.% insoluble in sulfuric acid									
	Sample directly pre-oxidized		Sample pre-extracted with n-hexane and pre-oxidized		Sample pre-leached with oxalic acid and pre-oxidized		Sample pre-extracted, pre-leached and pre-oxidized		Sample pre-leached, pre-extracted and pre-oxidized	
	NiMo1	NiMo 2	NiMo1	NiMo 2	NiMo1	NiMo 2	NiMo1	NiMo 2	NiMo1	NiMo 2
Support										
Al_2O_3	21	15	19	12	19	12	18	11	18	11.5
Active phase										
MoO_3	25	14	11	6	9	5	5	3	5	3
NiO	5	2	2	1	1	0.5	0.5	< 0.1	0.5	< 0.1
SO_3	20	11	6	5	5	4	3	3	4	2
Additives										
SiO_2	100		100		100		100		100	
P_2O_5	82	73	67	61	60	55	55	51	57	53
Foulant elements										
Fe_2O_3	5	5	5	3	5	3	2	1	3	1
CaO	0	0	0	0	0	0	0	0	0	0
As_2O_3	11	7	4	2	3	1	2	0.5	3	0.5
Whole sample	32.0	21.0	23.2	15.1	22.3	15.0	20.0	13.1	20.5	13.3

in sulfuric acid (~30 wt.% less). Si (fully insoluble), P and Al are still the main components of the insoluble matter, but the amount of insoluble active phase components markedly decreased. Al was slightly more leached. Both procedures, whatever the order, reduced even more the amount of insoluble matter in sulfuric acid (~40 wt.% less).

Removal of soluble coke (more hydrogenated) reduces risk of ignition of insoluble coke.[23,25,26] The presence of soluble coke and foulant elements (over the catalyst surface) may favor local flashing zones, thus forming refractory compounds.[2,28] Component interaction may occur on overheating. $Ni_3(PO_4)_2$ and $NiSiO_3$ were not solubilized in 9 mol L^{-1} sulfuric acid. $NiMoO_4$ was only sparingly soluble in this leachant. As seen in Table 7, losses of active phase and support components are higher in the NiMo catalyst with higher Si and P amounts (Table 1). This fact strongly suggests that Si and P act as a sink for metals when there are overheating zones during coke removal.[6]

The effect of catalyst composition and pre-treatment level on foulant elements is much less important. These elements were already soluble in the sample directly oxidized. Their location (at the surface of the catalyst) may explain at least partially this phenomenon.

A three-step pre-treatment increases chemicals consumption, generates more final wastes and is more energy consuming. On the other hand, metal losses during leaching with oxalic acid are much lower than the additional amounts leached by sulfuric acid. The additional metals recovery may not compensate this deep pre-treatment but the catalyst composition may justify such procedure: the presence of high amounts of Si, P (and also V[2,14]) tends to favor the multi-step pre-treatment process due to the considerable additional recovery of valuable metals from these samples.

CONCLUSIONS

A good pre-treatment procedure is more than coke removal under controlled conditions. Two previous steps before coke burning – extraction of soluble coke and removal of foulant elements by oxalic acid – greatly reduced losses of valuable metals leachable by sulfuric acid after burning insoluble coke. The amount of insoluble matter in this acid fell from 21-32 to 15-23 wt.% after one step, and to 13-20 wt.% after both steps. The main elements present in the insoluble residue are aluminum, phosphorus and silicon.

Leaching with oxalic acid was only noticeable for iron. About 50 wt.% of this element (0.8 wt.% of the overall catalyst mass) was removed. The concentration of the oxalic acid, time and temperature must be controlled in order to avoid excessive leaching of metals from the active phase (> 1 wt.%). It is better to remove partially the foulant elements rather than to obtain a high removal with a simultaneous considerable leaching of valuable metals. Soluble coke corresponds to a small fraction of overall coke (3 wt.%, 0.2-0.3 wt.% of the overall catalyst mass). Despite the low amounts of iron and soluble coke removed, both components have a markedly influence on metals leaching of the oxidized catalyst.

Although a three-step pre-treatment is more laborious, it is clear that this procedure improves metals recovery from spent catalysts, particularly those with high Si and P amounts. The catalyst composition and the type of the feedstock treated probably will influence the behavior of the pre-treatment. The amounts of the elements deposited on the catalyst surface will determine the adjustment of experimental parameters in order to prepare the sample for coke burning and leaching with strong acids. Other spent catalysts from different processes are being studied in this context.

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