



Hydrometallurgical route to recover molybdenum, nickel, cobalt and aluminum from spent hydrotreating catalysts in sulphuric acid medium

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ABSTRACT

This work describes a hydrometallurgical route for processing spent commercial catalysts (CoMo and NiMo/Al₂O₃), for recovering the active phase and support components. They were initially pre-oxidized (500 °C, 5 h) in order to eliminate coke and other volatile species present. Pre-oxidized catalysts were dissolved in H₂SO₄ (9 mol L⁻¹) at ~90 °C, and the remaining residues separated from the solution. Molybdenum was recovered by solvent extraction using tertiary amines. Alamine 304 presented the best performance at pH around 1.8. After this step, cobalt (or nickel) was separated by adding aqueous ammonium oxalate in the above pH. Before aluminum recovery, by adding NaOH to the acid solution, phosphorus (H₂PO₄⁻) was removed by passing the liquid through a strong anion exchange column. Final wastes occur as neutral and colorless sodium sulphate solutions and the insoluble solid in the acid leachant. The hydrometallurgical route presented in this work generates less final aqueous wastes, as it is not necessary to use alkaline medium during the metal recovery steps. The metals were isolated in very high yields (>98 wt.%).

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1. Introduction

Hydrotreatment (HDT) is a group of catalytic hydrogenation reactions, which saturates olefinic and aromatic hydrocarbons, eliminates heteroatoms (such as nitrogen, sulphur and oxygen) and even metals in the feedstock to be treated. HDT is one of the most important catalytic processes and its catalysts correspond to about 10% of the worldwide catalyst market [1]. HDT has been extensively employed for processing heavy feedstocks (such as Chinese, Venezuelan and Brazilian petroleums), as well as to improve the quality of end products and intermediates for reforming and fluid catalytic cracking processes (FCC).

At present environmental directories impose severe restrictions concerning gas and particle emissions from refineries and fuels. These directories require the improvement of the petroleum refining (higher impurities removal). Sulphur removal (hydrodesulphurization) is essential to obtain more acceptable fuels for environment [2]. The maximum allowed sulphur content in diesel is 10 ppm in Europe (from 2008 [3,4]), 15 ppm in the USA (since 2006 [4]) and 50 ppm in Brazil (since 2007 [5]).

The most familiar HDT catalysts are CoMo, NiMo and NiW supported on alumina (Al₂O₃), normally modified by additives

that improve activity towards some HDT reactions (hydrogenation, cracking) or thermal resistance during its lifetime [1,6,7]. The increasing severity of the environmental directories concerning gas emissions (NO_x, SO_x, etc.) has been stimulating the development of a new generation of more efficient catalysts and the proposal of less drastic HDT conditions concerning energy and hydrogen consumption [1,8]. The studied parameters include: support preparation, inclusion of additives (P, B, Si, Mg, Ti, Pt, etc.), active phase deposition method [3,9,10] and manufacture of non-supported NiMo and CoMo samples of high surface area.

The North-American Environmental Protection Agency (EPA) [11,12] states that spent HDT catalysts may be pyroforic, spontaneously combustible and release toxic gases. The presence of sulphur is responsible for their flammability as its oxidation releases heat along the organic matter present. The presence of polyaromatic compounds in the coke deposited on the surface classifies these catalysts as a carcinogenic material. This situation is reinforced should nickel is present, since this metal is also carcinogenic to man. Although spent refinery catalysts correspond to about 4 wt.% of its overall waste [6,8], they are classified as one of the most dangerous wastes generated in petroleum refineries. Spent *in natura* HDT catalysts have proven to contain high amount of heavy metals (Ni, Co, Mo) that can be leached by water [13,14]. Leaching of catalysts in USA follows the toxic characteristic leaching procedure (TCLP) from the “American Society for Testing Materials”, and is based on the maximum amounts of elements in drinking water

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[19]: 7 ppb of Mo, 7 ppb of V, 0.3 ppm of Fe, 13.4 ppb of Ni and less than 0.7 ppb of Co. If one of the sample components surpasses 100 times the corresponding limit, the spent catalyst is a dangerous waste.

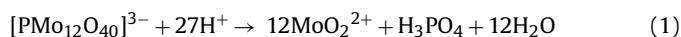
More than 90% of the European chemical industries [15] consider that definitive solutions for the spent catalyst must have been developed until 2012. The budget for this purpose and other refinery environmental challenges is US\$ 1.2 trillion (period 1997–2012). In USA the budget for the same purposes reaches US\$ 1.8 trillion (until 2015) [12]. It is expected that the greater severity of HDT reactions in the near future will increase generation of spent HDT catalysts [16].

The Resource Conservation and Recovery Act (RCRA) states [17] that a spent HDT catalyst must be previously oxidized at high temperatures (roasting) before sending it to an industrial dump because it is necessary not only to remove organic matter, but also insolubilize inorganic components. Incineration of spent catalysts is not a suitable practice [18] as this material has a low heat of combustion, thus requiring auxiliary fuel in order to ensure a full insolubilization of all its components.

Recovery of metals from spent catalysts depends on several factors: the nature of the sample (chemical composition) and the treated feedstock, the price of metals, the environmental directories, the distance between the refinery and the recycling industry and the operational costs [16,19]. Since the cost of transportation and disposal in industrial dumps, the severity of environmental directories, and the price of some metals (particularly cobalt) [20] have been rising, spent catalysts have been recognized as a secondary source of valuable metals [16,21–24]. This research field is very dynamic since the composition of a given catalyst may vary with time. Hydrometallurgical recovery routes require the maximum solubilization of the sample in an appropriate medium for the other central step, the separation of solubilized elements. For this purpose, it is necessary to pre-treat the sample in order to remove coke and other volatile species present. This step “cleans” the catalyst surface, thus reducing losses of recoverable metals by physical blocking. Care must be taken to avoid catalyst ignition during pre-treatment, thus forming refractory oxides that are difficult to solubilize in the leaching medium.

Extraction of metals with extractants dissolved in organic solvents has been gaining importance since the 1990s. Organophosphorous compounds are widely used [25–27] for treating effluents and leachates, especially in sulphuric acid medium. Extraction of molybdenum [28,29] with amines and organophosphorous compounds is possible in low pH (normally 1–2). Fe, Co, Ni and Al are not extracted. In pH below 2 MoO₂²⁺-type species predominate, whereas neutral or anionic species are dominant above this pH [30].

Molybdenum recovery presents a critical challenge—its separation from phosphorus, which is normally found as a support additive (this problem is also found when Mo is recovered as a by-product from uranium ores [31]). Mo forms heteropolyanions with P, V, Si and As. The challenge is to decompose them, for example:



Small amounts of a strong mineral acid play this role provided pH is below 2. It is easier to decompose phosphomolybdates than vanadomolybdates, whereas silicomolybdate [SiMo₁₂O₄₀⁴⁻] species are only decomposed in concentrated sulphuric acid [31]. Therefore, Mo recovery by solvent extraction depends on the presence or absence of P, Si, etc., and the settlement of experimental parameters (specially the concentration of the acid during sample leaching) to take into account the presence of such additives. In general, the influence of P on Mo recovery from spent catalysts is not discussed. Re-extraction of this metal to the aqueous phase is normally performed with NH₄OH [28,30].

Solvent extraction appears to be the most cited technique for separation of Ni or Co from complex matrixes. About 50% of the Co produced in the western world comes from solvent extraction [32]. In general, extractions are performed under pH between 4 and 7.5 [33], although there are some examples where these metals are extracted in ammonia solution [34]. Co is usually extracted in lower pH than Ni [35]. Ni separation is difficult as the ionic strength increases as pH increases [36]. Minerals, batteries, metallic nodules and standard solutions are the basic materials employed in these studies, where sulphuric acid is by far the most employed one. Under the pH for Ni/Co extraction Al precipitates (fully or partially). It would be suitable to recover Ni/Co by solvent extraction in lower pH (<2), which appears to be difficult with the present solvent extraction technology [37,38] (many stages are necessary to reach a high recovery of those elements).

This work presents a hydrometallurgical route for processing spent HDT catalysts in sulphuric acid solution. Recovery of components of the active phase (Mo, Ni or Co) and of the support (Al) was performed by a combination of several separation techniques in acid solution. The goal is to generate less final wastes as possible. The overall route present in this work was compared to those presented in the literature for the same catalysts.

2. Experimental

2.1. Catalysts

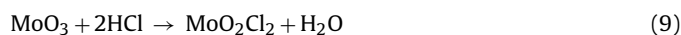
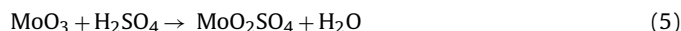
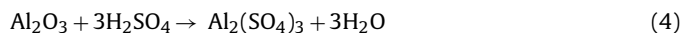
Spent NiMo and CoMo/Al₂O₃ catalysts were employed (5 mm cylinder extruded, 1.2 mm diameter). Chemical analyses are presented in Table 1. The catalysts were employed for at least 3 years in diesel/gasoline hydrotreaters in Brazilian refineries. For one of the CoMo catalysts this table also presents the analysis of its fresh sample. Samples were not ground and were dried at 110 °C for 2 h.

2.2. Pre-oxidation of samples

Samples were placed in identical ceramic crucibles. Since they were not ground, catalyst height in the crucible was fixed at 5 mm. Pre-oxidation was performed in a furnace following two heating rates: (i) 10 °C min⁻¹, from room temperature up to 500 °C (final time 5 h), according to previous studies in our laboratory [39,40]; (ii) 3 °C min⁻¹, from room temperature up to 500 °C (final time 5 h). The roasted mass was cooled down in the furnace and transferred to a dessicator before running the experiments. Chemical analyses of pre-oxidized samples are given in Table 1.

2.3. Leaching procedure

Sulphuric and hydrochloric acid solutions were tested, according to literature studies. The stoichiometric amount of each acid was calculated according to the following reactions:



From data of Table 1, the theoretical concentrated sulphuric acid/catalyst mass ratio is approximately 2.1:1 for all samples (or

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