

## Leaching of heavy metals under ambient resembling conditions from hydrotreating spent catalysts

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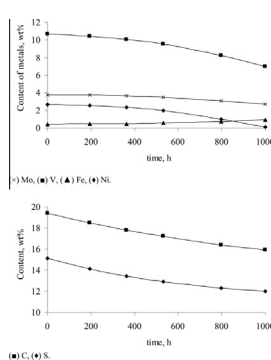
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### HIGHLIGHTS

- ▶ Metals leaching were simulated over a commercial spent hydrotreated catalyst.
- ▶ At conditions similar to an environmental situation, leaching of Ni, Mo and V occurs.
- ▶ The presence of sulfur and coke species is a key factor for metals leaching.
- ▶ Unattended spent hydrotreated catalysts represent a risk for the environment.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Spent hydrotreating catalysts are not inert to air, humidity and temperature, as the combination of these factors may gradually leach metals from the catalyst causing contamination of land and groundwater. In order to investigate the combined effect of ambient variables on metals leaching, a spent hydrotreating catalyst is placed in a tin can heated at 40–50 °C and then treated for 1000 h under a continuous flow of wet air. Said spent catalyst contains 10.68 wt.% V, 0.43 wt.% Fe, 2.67 wt.% Ni and 3.78 wt.% Mo as well as 14.7 wt.% coke and 19.4 wt.% sulfur, the latter basically in the form of metallic sulfides. During the leaching experiment, samples of spent catalyst are taken at different times to track the evolution of metals and coke/sulfur content. At the end of the test, even though relatively low temperatures are used, Ni is fully removed, Mo and V are partially extracted (around 25% for each metal) while the Fe content increases. Practically no leaching of metals is observed on the sulfur/coke-free fresh catalyst subjected to an identical experimental procedure. The presence of sulfur and coke on the spent catalyst clearly enhances metals leaching. The sulfur oxides produced from the oxidation of metallic sulfides with air, in combination with water, results in the formation of acidic species, which have a strong positive influence in leaching metals from the spent catalyst.

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### 1. Introduction

At present, environmental regulations for automotive fuels specifications and atmospheric emissions are evolving towards more severe limits. This trend is clearly opposite compared with

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the tendency related to the quality of the crude oils processed worldwide in terms of heaviness and contents of sulfur, nitrogen and metals [1]. In the oil refining context, the consumption of catalysts for hydrotreating heavy oil fractions, a process used extensively for removing sulfur, nitrogen and metals, has grown drastically. The website of the Petroleum Industry Research Institute reports that, to the date, the worldwide process capacity of hydrotreating plants is reaching 900 million tons per year [2].

Projections on catalyst demand indicate that it will continue increasing at a rate of 6% annually in the coming years [3–5].

Hydrotreating catalysts are composed of Ni and Mo oxides as well as other promoters, all these supported on a matrix consisting of  $\gamma$ -alumina. During the hydrotreating of heavy oil fractions, the catalyst deactivates gradually by the deposition, over the catalytic surface, of both metallic and non-metallic species, mainly V, Ni, sulfur and carbonaceous deposits designated coke [6–10]. Deposition of Fe on the catalyst surface also occurs since corresponding metal oxides are released due to the corrosion of the vessels and equipment, for instance, tanks, process pipelines and heat exchangers, used in the process. The presence of these contaminants combined with a gradual sintering of the matrix owing to thermal effects leads to an irreversible deactivation of the catalyst. After around 3 years, a value that corresponds to the average operating cycle of the catalyst, it has to be discharged out of the reactor and replaced by a fresh one [11]. The discharged catalyst, denoted as spent catalyst, is considered by Environmental Protection Agency (EPA) as a hazardous material [12] since sulfur and Fe combines chemically to produce the corresponding iron sulfides, which are pyrophoric, namely, may ignite spontaneously in the presence of air, coke and sunlight [13]. The problem related to the storage of spent catalyst is a real concern for refineries as the amount of catalyst to be handled is very large. For instance, a typical hydrotreating unit processes around 30,000 barrels per day requiring of about 50 tons of catalysts. Considering that a large scale refining company hydrotreats about 1 million of barrels per day, the generation of nearly 500 tons per year of spent catalysts is expected.

Procedures for handling and storing spent hydrotreating catalysts are diverse as reported in the open literature [14]. Commonly, when the unit has shut down for a catalyst replacement, the spent catalyst is discharged through bleeding pipes located at the bottom of the reactor. A flexible sleeve was used to download the catalyst directly into a screening machine. The latter sieves the catalyst particles into different sizes removing fines and the bulky spheres of  $\gamma$ -alumina from the “main catalyst”. All these maneuvers for catalyst handling are performed under inert gas atmospheres wherein nitrogen or  $\text{CO}_2$  are commonly employed. Sometimes when the screening machine is out of operation, the catalyst is placed on the floor, on a tarp, for a further broad separation and classification. The maneuvers of separation and sorting can take from hours to several days. As the attention of the plant operators is focused on loading the new catalyst into the reactor for restarting its operation, activities for proper spent catalyst storage are no longer a priority.

For the spent catalyst storage, many alternatives are available, most of them using procedures that involve the usage of metal containers, more specifically bins or metallic drums. The use of the former is highly recommended due to their higher capacity. Bins are, however, rented generating additional costs to the catalyst unloading operation. Because the spent hydrotreating catalyst has a very low commercial value in contrast with other catalyst containing Pt or Pd, its storage is usually accompanied by relatively high expenses. Most of refineries store spent catalyst in metallic drums equipped with a plastic bag to avoid contact with air as well as humidity, and then placed in protected areas such as warehouses [15]. Nonetheless, when the plastic bag is broken due to an incorrect handling and when drums are not in a warehouse, the spent catalyst may be exposed directly to the atmosphere, namely to air, humidity and sunlight. Under these conditions, catalyst may self-ignite to produce gaseous products that, in combination with water, metal leaching is favored.

This paper presents results of the experimental leaching of heavy metals contained in a sample of commercial spent hydrotreating catalyst. Thus, in order to investigate what occurs when the spent catalyst is directly exposed to ambient, particular conditions

of temperature, air flow rate and humidity are selected. To indirectly examine the effect of the coke and sulfur contained in the spent catalyst sample on the metals leaching, a fresh catalyst is also tested at identical conditions.

## 2. Experimental

### 2.1. Catalysts

Samples of fresh and spent hydrotreating catalyst were utilized in the experimentation. Some physical properties of the fresh catalyst are as follows: specific surface area =  $320 \text{ m}^2/\text{g}$ , pore volume =  $0.85 \text{ cm}^3/\text{g}$ , apparent bulk density =  $0.85 \text{ g}/\text{cm}^3$ . Corresponding values of the spent catalyst are  $75 \text{ m}^2/\text{g}$ ,  $0.24 \text{ cm}^3/\text{g}$  and  $1.27 \text{ g}/\text{cm}^3$ , respectively. The diminution in the textural properties of the catalysts is the result of a gradual sintering of the catalyst support as well as metals and coke accumulation. The increase in the density of the spent catalyst compared with that of the fresh sample is a consequence of the metals deposition in the former.

The fresh catalyst, which is originally formulated using Ni and Mo as active metals supported on  $\gamma$ -alumina, was employed for comparison purposes. The composition of the spent catalyst is more complex than that of the fresh sample as a significant amount of sulfur and coke deposits gradually on the catalyst surface while processing heavy oil fractions containing hetero-atoms of sulfur in industrial hydrotreating plants. In addition, heavy oil fractions also contain organometallic compounds of Ni and V, which deposit progressively on the catalyst surface as well. The presence of such metallic species causes irreversible deactivation by covering and then blocking the catalyst active sites. The content of metals, coke and sulfur of spent and fresh catalysts are presented in Table 1.

### 2.2. Characterization of catalysts

Characterization of catalyst samples was first focused on conducting a compositional analysis which, at the end, is aimed at tracking the evolution of the content of metals, coke and sulfur, with time. The amount of metals contained in the catalysts was quantified by Optical Emission Spectroscopy using a Perkin Elmer 7300 DV Inductively Coupled Plasma (ICP) Spectrometer in accordance with method ASTM-D-5185-09. Prior to the analysis to determine the metallic content of the samples, they were calcined at  $500 \text{ }^\circ\text{C}$  for 4 h to remove carbon and volatile materials. A given amount of dry catalyst was digested with aqua regia to extract the metals from the sample. An aliquot of this dissolution is finally analyzed.

The quantity of carbon and sulfur on the spent catalyst sample was determined by oxidative combustion followed by elementary analysis of the resulting gases using a Thermal Conductivity Detector equipped with a Bari computer. Such analyses were performed in accordance with standard ASTM methods, the D-1552-08 for

**Table 1**  
Concentration of metals, sulfur and carbon in the fresh and the spent catalyst samples under investigation.

	Fresh catalyst	Spent catalyst
<i>Metallic species, wt.%</i>		
Ni	4.23	2.67
V	–	10.68
Fe	–	0.43
Mo	6.95	3.78
<i>Non-metallic species, wt.%</i>		
C	–	19.4
S	–	14.7

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