

Catalyst Deactivation during Hydrotreating of Maya Crude in a Batch Reactor

S. K. Maity,* V. H. Pérez, J. Ancheyta, and Mohan S. Rana

Instituto Mexicano del Petróleo, Eje Central Norte Lázaro Cárdenas 152, Col. San Bartolo Atepehuacan, México D. F. 07730

Received October 4, 2006. Revised Manuscript Received November 27, 2006

The deactivation of a hydrotreating catalyst is investigated in a batch reactor by using Maya heavy crude as a feed. A reference catalyst NiMo supported on gamma alumina having wide pore diameter is used to evaluate hydrodemetallation (HDM) and hydrodesulfurization (HDS) activities. It is found that, with increasing contact time, the conversion and deposits increase. The pore size distribution results show that surface area and total pore volume significantly reduce on the spent catalysts due to coke deposits. However, loss of these properties is reversed upon regeneration of the spent catalysts. It is observed from SEM study that coke preferably deposits on the pore mouth whereas vanadium is more evenly distributed throughout the catalyst particles. These deposits cause the deactivation of HDM activity; however, the reason for the loss of HDS activity is only the presence of metal deposits which may cover active sites.

1. Introduction

Catalyst is deactivated very rapidly during hydrotreating of heavy oils or residue. The catalysts are exposed to highly severe conditions, and this together with the tendency of coke formation and metals deposition dictates the catalyst deactivation. It is a general practice in a refinery that catalyst deactivation is compensated by raising the temperature constantly, i.e., the higher the temperature the higher the reaction rate that compensates the loss of activity. The catalyst deactivation occurs by deposits of carbonaceous particles along with metal sulfides. Carbon or coke is deposited very rapidly within a few hours of run time, and then, the deposition reaches a steady state. Coke buildup again increases at the end of the run where the reaction temperature is high. However, metals are progressively deposited throughout the hydrotreating process. The amount of coke and metals buildup depends on the feed properties and operating conditions.^{1,2}

The “soft” coke which is formed at the initial stage of reaction is the principal cause of a loss of micropores and consequently surface area. It approximately reduces one-third of the porosity,³ whereas the “hard” coke which is formed in a later stage of reaction and metal sulfides take up the remaining porosity. At the initial stage, coke is mostly deposited on the bare surface area. Its interaction with the surface is much stronger when the feed contains more aromatic hydrocarbons. Heavy oil generally contains oils, resins, and asphaltenes. During hydrotreating, oil and resin fractions are converted to smaller fragments, and this causes a decrease of the solubility of asphaltene. Therefore, asphaltenes are precipitated on the catalyst surface and block the catalyst pore. When the catalyst pore is small, coke is deposited on the pore mouth, whereas it penetrates into the pore cavity when the catalyst pore diameter is comparatively large.

The presence of vanadium and nickel is of particular concern because of the deactivation effect during hydrotreating. The metals are commonly distributed between porphyrin and non-porphyrin types of structures.^{4–6} These metal containing compounds are deposited into the catalyst during hydrotreating and cause deactivation. Deactivation by metals is irreversible. Vanadium, due to its higher reaction rates, concentrates at the surface of the catalyst, whereas nickel is distributed more evenly throughout the catalyst pellet.^{7–9} Vanadium can decorate the edge of a molybdenum disulfide slab just as a nickel or cobalt promoter can. However, vanadium displaces nickel from the edge sites on the molybdenum slab and is then a source of deactivation since promotion by vanadium is less than that by nickel.¹⁰

There are several publications regarding the deactivation of a hydrotreating catalyst. Some of the researchers assumed that rapid coke deposits might cause initial deactivation of the catalysts, while others reported that the deposition of metals should also be considered for initial deactivation. It was also stated that deactivation might be the composite effect of metals and coke deposits, and it was not easy to distinguish quantitatively between deactivation by coke and by metals. However, in this study, we have tried to identify quantitatively the cause of deactivation by coke and metal depositions during hydrotreating reactions. In this regard, we have used batch reactor to study hydrodemetallation (HDM) and hydrodesulfurization (HDS) activities for Maya heavy crude.

2. Experimental Details

2.1. Characterization of Catalyst. BET specific surface area, pore volume, and pore size distribution of fresh, spent, and

* Corresponding author. Tel.: 52-55-91758422. Fax: 52-55-91758429. E-mail: skumar@imp.mx.

(1) Trimm, D. L. *Catalysts in Petroleum Refining* 1989; Trimm, D. L., Ed.; Elsevier: Amsterdam, 1990; p 41.

(2) Furimsky, E.; Massoth, F. E. *Catal. Today* **1999**, 52, 381.

(3) Newson, E. *Ind. Eng. Chem. Process Des. Dev.* **1975**, 14, 27.

(4) Ohtsuka, T. *Catal. Rev—Sci. Eng.* **1977**, 16 (2), 291.

(5) Agrawal, R.; Wei, J. *Ind. Eng. Chem. Process Des. Dev.* **1984**, 23, 505.

(6) Agrawal, R.; Wei, J. *Ind. Eng. Chem. Process Des. Dev.* **1984**, 23, 515.

(7) Ware, R. A.; Wei, J. *J. Catal.* **1985**, 93, 100.

(8) Ware, R. A.; Wei, J. *J. Catal.* **1985**, 93, 122.

(9) Ware, R. A.; Wei, J. *J. Catal.* **1985**, 93, 135.

(10) Mitchel, P. C. H. *Catal. Today* **1990**, 7 (4), 439.

regenerated catalysts were measured by nitrogen adsorption at 77 K (Quantachrome Nova 2000). Metal contents of the spent catalysts were determined by an atomic absorption spectrometer (Thermo-electron model Solaar AA). The percentage of carbon was also measured on spent catalysts. The spent catalysts were washed with hot toluene by the Soxhlet process and dried at 110 °C before carbon and metal analyses. Coke is defined in this work as the carbon content on spent catalyst. The radial depositions of coke and vanadium on the spent catalysts were measured by a scanning electron microscope (SEM), model XL30 ESEM, Philips.

The total metals in the feed and products were measured by atomic absorption (Thermo-electron model Solaar AA). Sulfur was analyzed by X-ray fluorescence (HORIBA model SLFA-2100/2800).

2.2. Catalyst Activity Test. A 5 g of fresh catalyst was sulfided ex-situ for each experiment of study activity. An atmospheric unit was used for sulfidation. In this unit, hydrogen was passing through a container having CS₂. The saturated mixture of CS₂ and hydrogen passed through the reactor. The sulfiding conditions for the activation of catalyst were as follows: temperature, 400 °C; atmospheric pressure; duration of sulfidation, 3 h; hydrogen flow, 40 mL/min.

The catalytic activity was studied in a batch reactor. A 200 g of Maya heavy crude was taken into the reactor vessel (1 L capacity). The sulfided catalyst was transferred into the reactor in nitrogen atmosphere very quickly so that the catalyst would not be in contact with air for a long time. The reactor vessel was properly tightened and checked for leakage. The reactor vessel was then purged two/three times with hydrogen gas so that there was no air left inside the reactor. Heating was started from room temperature to the required temperature at the rate of 3 °C/min. Stirring was started when the temperature reached the set point (380 °C) and the time was noted as the beginning of the reaction at this point. The experimental conditions of the batch reactor were as follows: temperature, 380 °C; total pressure, 100 kg/cm²; catalyst weight, 5 g; Maya crude, 200 g; duration of reaction, 2–10 h; and stirring speed, 750 rpm. Products were separated from the catalyst after reaction, and metals and sulfur contents of the products were analyzed.

In another study, 15 g of catalyst was taken with 600 g of Maya crude and the reaction was studied over 6 h under the above maintained conditions. After the reaction, the catalyst was separated from the product. The spent catalyst was washed by the Soxhlet process mentioned above. This spent catalyst was divided in two parts: one part was directly used for activity testing and another part was used for regeneration. For the former, an appropriate amount of spent catalyst (the amount of coke has been subtracted) was sulfided before the activity test. For the latter, an appropriate amount of spent catalyst was regenerated in a flow of oxygen at 550 °C for 5 h. After regeneration, the catalyst was sulfided and then evaluated. A fresh catalyst was also tested under similar conditions to compare the results obtained for spent and regenerated catalysts. In this case, the duration of reaction was 6 h.

3. Results and Discussion

3.1. Physicochemical Properties of Catalyst and Feed. A commercial NiMo catalyst supported on alumina was used in this work. It contains 10.66 wt % of MoO₃, 2.88 wt % of NiO, and 3.73 wt % of TiO₂. The pore size distribution of this catalyst (C0) is presented in Figure 1. The figure shows that the catalyst has a wide pore size distribution in all over the region. Its specific surface area, total pore volume, and average pore diameter are 137 m²/g, 0.529 cm³/g, and 155 Å, assuming a cylindrical pore model, respectively.

Maya heavy crude was used as a feed which contained 3.42 wt % sulfur and 322 wppm metals. The properties of this feed are given in Table 1.

3.2. Study of Catalyst Activity. Hydrodemetallation (HDM) and hydrodesulfurization (HDS) are studied at several reaction

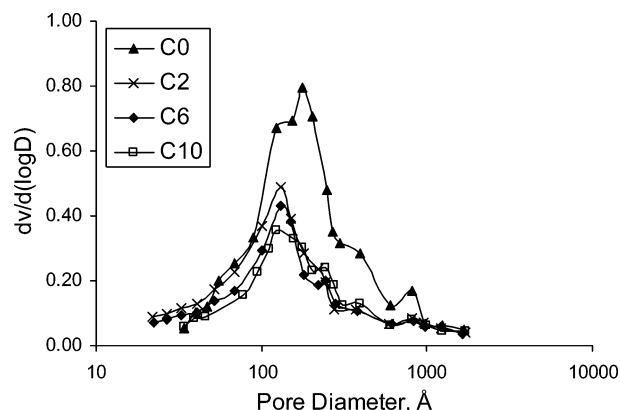


Figure 1. Pore size distribution of fresh and spent catalysts.

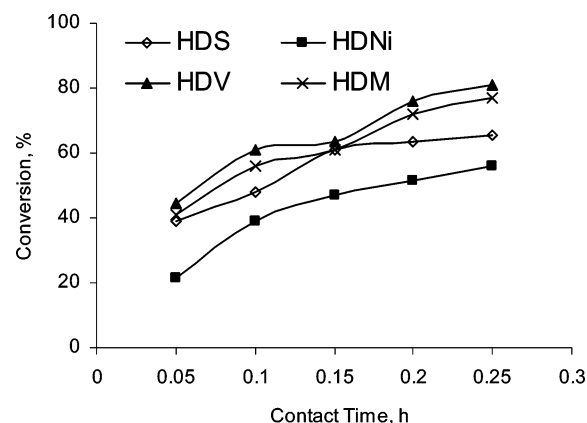


Figure 2. Effect of contact time on HDM and HDS conversions.

Table 1. Properties of Maya Heavy Crude

properties	Maya
API gravity	20.99
sulfur, wt %	3.42
nitrogen, wppm	3006
ramsbottom carbon, wt %	11.01
asphaltenes (in C ₇), wt %	12.26
Ni, wppm	52
V, wppm	270

times in the batch reactor, and the results are presented in Figure 2. In this figure, conversions are plotted against contact time which is calculated for a batch reactor by the following equation.¹¹

$$\text{Contact time} = \frac{(\text{Catalyst weight}) \times (\text{Total reaction time})}{\text{Feed weight}}$$

Figure 2 shows that both the HDS and HDM activities increase with increasing contact time. However, the increasing trends are different for the HDS and HDM reactions. The HDM conversion increases constantly with contact time, whereas the HDS activity increases up to 6 h and then become slow with further increase of the reaction time. During the reaction, H₂S and NH₃ are produced and these gases accumulate inside the reactor. With reaction time, the concentrations of these gases increase at the expense of reactive hydrogen. It is known that these gases have an inverse effect on hydrodesulfurization, since active sites for HDS also absorb H₂S and NH₃. However, the effect of H₂S on HDM is not severe. Some of the studies also proved that the increased partial pressure of H₂S had a beneficial effect on HDM.^{12,13} These may be the reason in this case for

(11) Gualda, G.; Kasztelan, S. *J. Catal.* **1996**, *161*, 319.

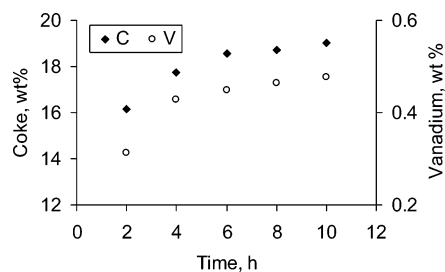


Figure 3. Coke and vanadium deposits on spent catalysts.

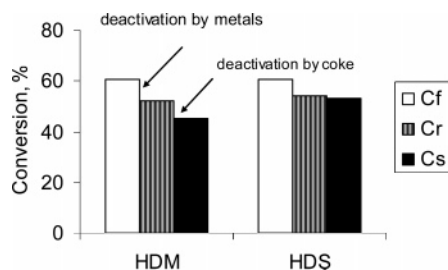


Figure 4. HDM and HDS conversions of fresh (f), spent (s), and regenerated (r) catalysts.

the higher increment of HDM activity compared to HDS with reaction time.

Vanadium and coke deposits on the spent catalyst are presented against the time of reaction in Figure 3. Both deposits increase with the time of reaction. The catalyst prolong contacts with the feed in a batch reactor, which means more conversion and more deposits. The rates of deposits are higher initially, particularly from 2 to 4 h, and after that, they slow down. The effect of deposits on the pore size distribution can be seen from Figure 1. These series are designated as CX, where X represents the total reaction time. For comparison, the pore size distribution of the fresh catalyst is also given in this figure. It indicates that the total pore volume of the catalyst constantly decreases with the time of operation. Compared with fresh catalyst, the specific surface area of the spent catalyst C10 is reduced around 30% by deposits over 10 h of reaction.

In another study, HDM and HDS activities of fresh, spent, and regenerated catalysts are evaluated under similar conditions, and the results are presented in Figure 4. Losses of both HDM and HDS activities are found in spent catalyst over 6 h of reaction. After regeneration of spent catalyst, HDM conversion gains some activity, while HDS conversion cannot be changed. During the hydrotreating reaction, coke and metals are deposited on the catalyst and this causes catalyst deactivation. Both coke and metals almost equally contribute to the loss of HDM activity. However, the loss of HDS activity only occurs by metals deposit. Therefore, the mechanism of the removal of metals and sulfur compounds from feed do not follow the same way.

The pore size distributions of spent and regenerated catalysts are compared with that of the fresh catalyst in Figure 5. Although a drastic change of pore volume is observed in spent catalyst, it can be reversed on regeneration. During regeneration, coke is left out of pores as carbon dioxide, but metals remain in the pores, showing that the changes of pore structure of the catalyst occur mainly due to coke formation, particularly at the initial stage of the hydrotreating reaction.^{14,15}

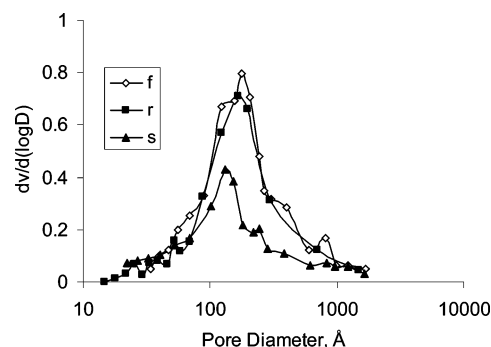


Figure 5. Comparison of pore size distributions of fresh, spent and regenerated catalysts.

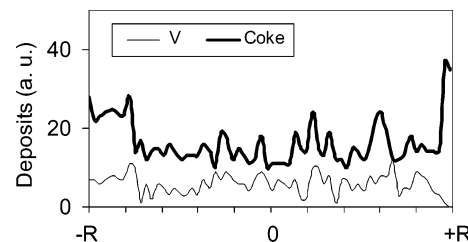


Figure 6. Radial distribution of coke and vanadium deposits.

The profiles of coke and vanadium deposits are also studied by SEM, and the radial distribution of these deposits for the catalyst C10 is presented in Figure 6. The maximum coke is deposited superficially on the catalyst particle, whereas vanadium penetrates more deeply into the interior of the catalyst particle, indicating that the size of coke particles is bigger than that of vanadium sulfide.

During early stages of hydrotreating of heavy fractions, coke is predominantly deposited on the external surface of the catalyst extrudates. In due course of operation, coke gradually penetrates into the interior portion of the catalyst. Therefore, deactivation can occur by both phenomena—pore mouth plugging and core poisoning—depending on the catalyst pore structure.^{16,17} On the other hand, metal sulfides, particularly vanadium and nickel sulfides, are constantly deposited, and due to their smaller size, these sulfides enter into the pore cavity. Therefore, the deactivation due to metal sulfides may occur by covering of interior active sites of the catalyst rather than pore mouth plugging when metal deposits are comparatively low. The smaller size of vanadium sulfide is further supported by our previous studies,¹⁵ where we could not find any detectable crystalline vanadium sulfide. In this work, it is considered that both coke and metal deposits are responsible for the deactivation of HDM activity. Gualda and Kasztelan¹¹ also observed that both coke and metal deposition deactivated HDM activity but metal deactivation was more pronounced over coke deactivation at the initial stage of operation.

The loss of HDS activity is caused only by metal sulfides. Metal bearing compounds in heavy crude are larger in size compared to the sulfur molecules. It is observed from SEM results that coke is preferably formed on the pore mouth whereas vanadium is more evenly distributed into the catalyst particle. Therefore, coke may hinder the entrance of metal compounds

(12) Bonné, R. L. C.; van Steenderen, P.; van Langeld, A. D.; Moulijn, J. A. *Ind. Eng. Chem. Res.* **1995**, *34*, 3801.

(13) Bonné, R. L. C.; van Steenderen, P.; Moulijn, J. A. *Appl. Catal. A: Gen.* **2001**, *206*, 171.

(14) Maity, S. K.; Ancheyta, J.; Alonso, F.; Rana, M. S. *Catal. Today* **2004**, *98*, 193.

(15) Maity, S. K.; Ancheyta, J.; Rana, M. S.; Rayo, P. *Catal. Today* **2005**, *109*, 42.

(16) Haynes, H. W.; Leung, K. *Chem. Eng. Commun.* **1983**, *23*, 161.

(17) Leung, K.; Haynes, H. W. *Chem. Eng. Commun.* **1984**, *31*, 1.

into the pore interior. However, sulfur containing compounds still may have a sufficient path to reach active sites of the catalyst. Hence, the deactivation of HDS by coke formation, particularly at the initial stage is not observed. The only deactivation of HDS is caused by metal sulfide. Several authors^{18,19} also observed that coke is preferentially deposited on the bare support not touching the active sites of catalyst. Zeuthen et al.²⁰ also reported that initial coke deposition had little effect on HDS activity.

Moreover, the coke which is formed during reaction is completely removed by regeneration of spent catalyst. Ammus et al.²¹ also reported that the coke formed at 70 h on stream is totally removed by regeneration; however, coke formed at a

longer period may not be totally removable and it causes permanent loss of pore volume and surface area.

4. Conclusions

The deactivation of Maya crude hydrotreating catalyst is investigated in a batch reactor. It is noticed that HDM and HDS conversions increase with increasing reaction time. Pore size distribution results show that, with increasing reaction time, specific surface area and total pore volume decrease due to coke formation. However, loss of these physical properties of the spent catalyst is reversed by regeneration of these catalysts. It is also observed from SEM study that coke is preferably deposited on the pore mouth, whereas vanadium is deposited into a more interior part of the catalyst particle. Coke deposition has little effect on HDS activity, particularly at the initial period of reaction, but both coke and metals deposits are responsible for the deactivation of HDM activity. Metals deposits may cover active sites of the catalyst and so cause the deactivation, whereas the deactivation by coke occurs by pore mouth plugging.

EF060495Z

(18) Dorn, J. V.; Moulijn, J. A. *Fuel Process. Technol.* **1993**, 35, 275.

(19) Fleisch, T. H.; Meyers, B. L.; Hall, J. B.; Ott, G. L. *J. Catal.* **1984**, 86, 147.

(20) Zeuthen, P.; Bartholdy, J.; Wiwel, P.; Cooper, B. H. In *Catalyst Deactivation*; Delmon, B., Froment, G. F., Eds.; Elsevier: Amsterdam, 1994; p 199.

(21) Ammus, J. M.; Androustopoulos, G. P.; Tsetseku, A. H. *Ind. Eng. Chem. Res.* **1987**, 26, 1312.