

## Deactivation of Catalyst during Hydrotreating Heavy Crude-Derived Residual

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### Introduction

Catalyst deactivation is one of the main concerns during hydrotreating (HDT) of heavy oil fractions. Loss of active sites is the main reason for catalyst deactivation. Three deactivation periods are identified during HDT of heavy fractions: (1) Deactivation by coke, which is mainly caused from asphaltenes, (2) Deactivation by metals, which is irreversible and whose rate depends on the metals level in the feed, and (3) Pore constriction and blockage, characterized by a very strong loss in activity, after which the plant has to stop operation.<sup>1</sup>

It is well-documented in the literature that coke is formed very rapid during first hours of time-on-stream, and catalyst deactivation by this carbonaceous material appears to rapidly reach a pseudo steady-state level, while deactivation by metals takes longer time period.<sup>1,2</sup>

Various authors have reported catalyst deactivation studies during HDT of oil fractions. Different feeds mainly derived from light crudes have been used for experiments and HDT of heavy residua has not received too much attention. The main goal of this paper is to analyze catalyst deactivation during HDT of a residue derived from Maya heavy crude oil.

### Experimental

All text were conducted in a high-pressure pilot plant described in detail elsewhere.<sup>3,4</sup> A residue obtained from atmospheric distillation of Maya heave crude was used as HDT feed. The main properties of this feed are: 8.5 API gravity, 4.7 wt% sulfur, 85 wppm Ni, 465 wppm V, 19.3 wt% asphaltenes. The catalyst was a NiMo commercial sample with the following properties: 175 m<sup>2</sup>/g SA, 0.56 cc/g PV, 127 Å MPD. Pore size distribution of this catalyst is 6.7 vol % 50-100 Å, 69.1 vol % 100-250 Å, 15 vol % 250-500 Å.

The catalyst was loaded to the reactor and in-situ activated by sulfiding with a hydrodesulfurized naphtha containing 0.8 wt% CS<sub>2</sub> at the following operating conditions: pressure of 54 kg/cm<sup>2</sup>, H<sub>2</sub>-to-oil ratio of 2000 ft<sup>3</sup>/bbl, temperature of 230°C, and liquid-hourly space-velocity (LHSV) of 3.2 h<sup>-1</sup>. The sulfiding time was 18 h.

Experiments were carried out at constant operating conditions, and catalyst deactivation was studied as a function of time-on-stream in the range of 0-196 h.

### Results and discussion

Variation of S in product against time-on-stream is shown in Figure 1. It is clearly observed that deactivation of catalyst is very rapid during first hours of the run, which is attributed to losses of SA and PV due to coke formation. Ni and V removals showed different behavior as seen in Figure 2. It indicates that the rate of metal deposition varies from metal to metal. This can be attributed to the differences in Ni- and V-porphyrin type of structure, since in the case of vanadium a perpendicular oxygen atom is linked to it, which forms strong bond with the catalyst surface, and nickel does not have this oxygen links. Another explanation can be that the rate of Ni deposit formation is strongly influenced by formation of V deposits.

SA of catalyst decreased from 175 to 108 m<sup>2</sup>/g while loss of PV was from 0.56 to 0.37 cc/g, which means around XX% and XX% of reduction, respectively. Deposition of coke in early period of run and consequently blockage of pores is the main responsible of these reductions.

Percentage of pore volume having pore diameter higher than 500 Å exhibited a very important reduction (XX%). Similar behavior but with slightly less reduction (70%) was observed with pores in the range of 250-500 Å. Percentages of pore volume having pore diameter 100-250 Å remained almost unchanged since they only decreased from 69.1 to 66.1 % (X% of reduction). Smaller pores (<100 Å) exhibited a notable increase in their percentages from XX.X to 24.5%, which is mainly due to the reduction of the percentage of pore volume having pore diameter higher than 100 Å, mainly those higher than 250 Å. This behavior in catalyst pore size distribution suggests that during pore blockage large pores may be totally or partially covered. The partially covered pores then became smaller pores. As consequence of all these modifications in pore size distribution MPD of catalyst showed an increase from 127 to 139 Å.

Coke and V deposited on the catalyst were of 15.5 and 2.8 wt% respectively. This coke deposition is mainly formed from asphaltenes.

## Conclusions

Catalyst deactivation during HDT of heavy residue is very rapid during first hours of time-on-stream due mainly to coke deposition. Removals of Ni and V showed different behavior during time-on-stream, which was attributed to an oxygen atom linked to vanadium and to the influence of V on rate of Ni deposit. Changes in pore size distribution suggest that during pore blockage large pores may be totally or partially covered contributing to increase smaller pores percentage.

## References

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