Catalyst Deactivation (HVGO's and Lighter feeds)

Part 2

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Introduction

In part 1 of this paper, which was published in the previous Catalysts Courier (no. 16), the effect of operating conditions on deactivation was discussed. In this article the effect of metals or other contaminants in the feedstock on the catalyst activity will be discussed.

Deactivation due to metals

If a feedstock contains metals like V, Ni, Si etc., the catalyst will be contaminated by these metals. The metals are usually present as organo-metal compounds. Ni, Fe, V and As are contaminants present in the crude oil. Other metals like Si and Pb are added in the form of anti-foaming agents (Si) and additives to gasoline (Pb). In the next sections the effect of the individual metals will be discussed. Unlike coke deactivation, metal deactivation is irreversible. The metals cannot be removed by regeneration.

Nickel and vanadium

Nickel and vanadium are present in the heavy fraction of the crude oil. Usually these metals are observed in fractions with a boiling range of over 500°C. Therefore, nickel and vanadium poisoning is only significant in HVGO's and residues (atmospheric and vacuum residue). In this article we will not cover residues, since this is a special subject on which abundant literature is available. Also the types of catalyst used in residue hydroprocessing deviate from 'normal' hydrotreating catalyst.

On regular hydrotreating catalysts, nickel and vanadium are only deposited on the edge of the catalyst particles. Therefore the capacity of these catalysts for nickel and vanadium is not very large, and limited to about 10%wt on catalyst. At this metal level the catalyst is almost dead. The maximum allowable concentration on catalysts is about 3-%wt.

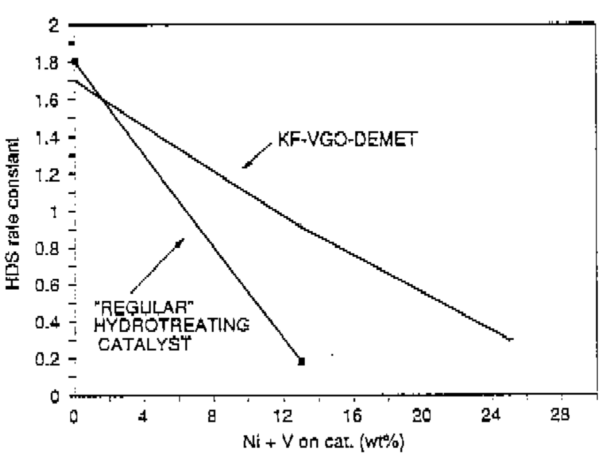


Figure 1: Effect of Ni + V on catalyst activity (conventional catalysts)

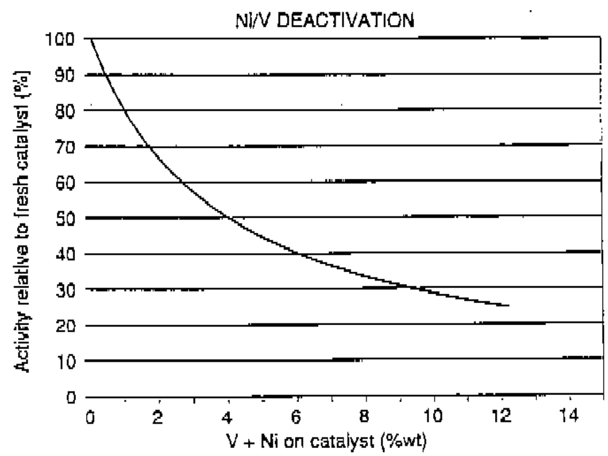
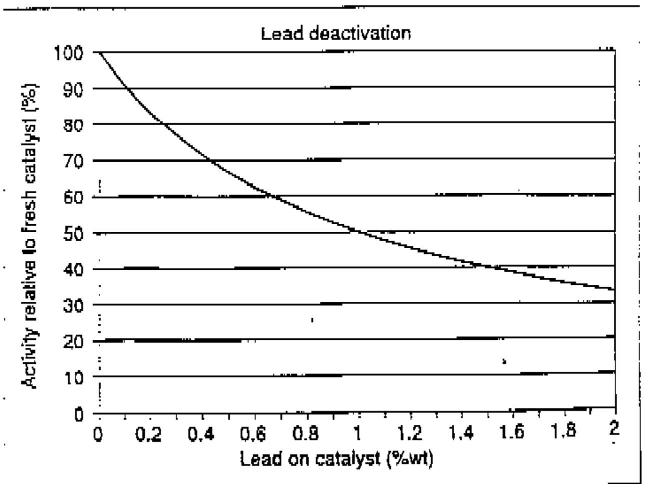


Figure 2: Effect of Ni + V on deactivation rate

Figure 1 gives the effect of Ni + V poisoning on the catalyst activity. As can be seen, metals have a large effect on the activity. Akzo Chemicals has developed a catalyst for VGO/distillate operation which can pick up much more metals (up to 25 %wt) than regular hydrotreating catalysts, and still has a very good HDS activity. This catalyst, Ketjenfine VGO-Demet, should be used in toplayers or in guard reactors, to protect the downstream catalyst from metal

Figure 3: Effect of Pb on catalyst activity



contamination, and can result in substantially longer cycles. In figure 2 the effect of metal pick-up on the HDS rate constant is plotted. Clearly it can be seen that the Ketjenfine VGO-Demet has a much higher tolerance for metals, thus resulting in a longer cycle. More information on the Ketjenfine VGO-Demet can be found in TI/HTC 87/99E. It is recommended to use the Ketjenfine VGO-Demet when the metal concentrations are exceeding 1.5 ppm Ni + V.

Lead deactivation

Lead is not naturally occurring in feeds. It is added to gasolines in the form of e.g. T.E.L. When processing slops over a hydrotreating catalyst, the T.E.L. is decomposed and the lead is deposited on the catalyst. Since T.E.L. decomposes easily, the lead profile in the reactor is usually steep.

Lead has a large effect on the catalyst activity. In figure 3 the relationship between lead on catalyst and the activity is plotted. Since lead is observed in naphtha's, and thus in reformer pretreaters, breakthrough of lead to the reformer should be avoided. Therefore it is recommended to run the pretreater at 300-320°C when processing lead contaminated feedstocks. Furthermore, the maximum amount of lead on the catalyst should not exceed 0.5%wt.

Arsenic deactivation

Arsenic occurs naturally in crude oils and is observed in naphtha's and light LGO's. It is an even more severe poison than lead. Figure 4 plots the effect on arsenic. The maximum allowable concentration is 500-1000 ppm on catalyst, depending on the operating severity.

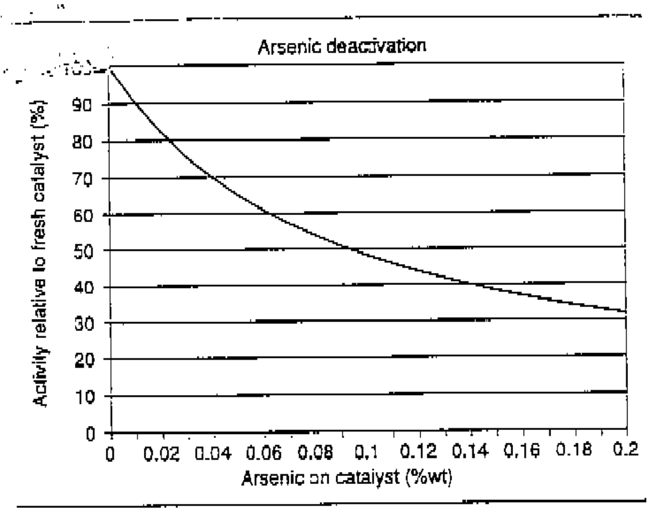
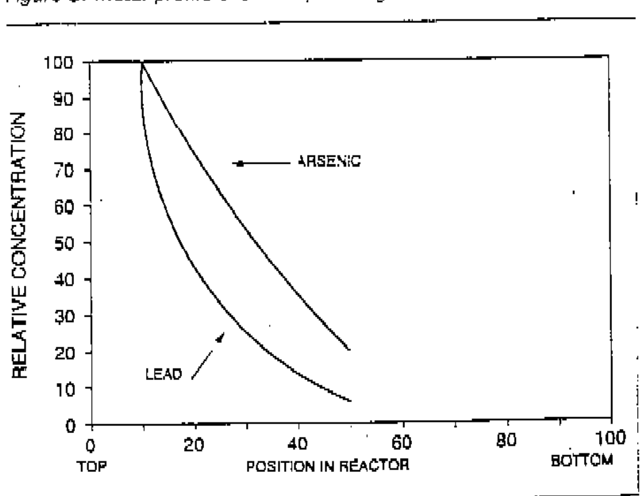


Figure 4: Effect of As on catalyst activity

Figure 5: Metal profile over a naphtha hydrotreater



In figure 5 the arsenic and lead profiles as measured in a naphtha hydrotreater are given. As can be seen, the profiles are steep and most of the contamination is present in the top of the reactor (30%). When unloading a Pb/As contaminated reactor, it is recommended to unload the first part of the catalyst bed over the top, in order to avoid mixing of contaminated and uncontaminated catalyst.

Si deactivation

Silicon originates from antifoaming agents. It is especially observed in coker naphtha's and sometimes in visbreaker naphtha. SiO_2 is not a very severe poison. A concentration of 15 %wt SiO_2 on catalyst can be tolerated during the cycle. Remarkable Si poisoning is more pronounced after regeneration. Most likely, when the coke is burned off, the SiO_2 is deposited on the active sites of a catalyst. When considering regeneration, a SiO_2 concentration of 3-4 %wt should not be exceeded. Akzo has developed special catalysts, Ketjenfine 844 and Ketjenfine VGO-Demet, which can protect down-stream catalysts against silica poisoning. These catalyst, when used as a toplayer, will protect the downstream catalyst. In TI-HTC 91/121E more information on the performance of these catalysts is given. In figure 6 the effect of silica on the activity before regeneration is given.

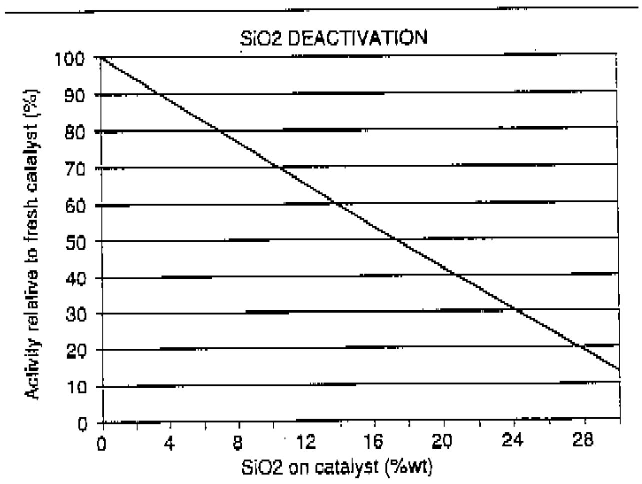


Figure 6: Effect of SiO_2 on catalyst activity

Conclusions

There are three main reasons for catalyst deactivation: Coke and metal deposition and changes in the active phase.

Coke deactivation is inevitable, but is accelerated by operating at low partial hydrogen pressures and high temperatures. In order to avoid unnecessary deactivation, one should try to run units at the minimum required severity, and at the maximum partial hydrogen pressure.

Operational up-sets can cause very rapid coke deposition and therefore a severe loss in activity.

The most frequently observed metals in oil fractions are nickel, vanadium, arsenic, lead and silicon. Nickel and vanadium are only observed in heavy cuts and arsenic, lead and silicon are mostly present in light cuts (naphtha). Special guard bed catalysts can protect against metals, by increasing the metal capacity of the catalyst system and therefore increase the cycle length.

Metal poisoning cannot be reversed by regeneration. Catalysts which are poisoned need to be replaced by fresh catalyst.