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PREFACE

We are very pleased to introduce the Proceedings of the 8th International Symposium on Catalyst Deactivation held in Brugge on October 10-13, 1999. In the almost regularly organized series of meetings, the location alternated between North America and Belgium : Berkeley, 1978; Antwerpen, 1980; Berkeley, 1985; Antwerpen, 1987; Evanston, 1991; Oostende, 1994; Cancun, 1997. This time a different location has been selected for the Belgian symposium 1999: Brugge, one of the most attractive medieval cities of the world. This could be done thanks to the invaluable organizational talent of Ms Rita Peys. We thank her for the magnificent job she did for this symposium.

The North American colleagues and we all gave different styles to each of these symposia, and selected programs with specific objectives. But in all cases, the aim was to develop the knowledge that the scientific community has of catalyst deactivation. There is a continuous progress in this area, but perhaps not so rapid as desirable for the general development of the science and applications of catalysis. There is certainly a consensus that a deeper understanding of the phenomena which cause catalyst deactivation will contribute to the development of catalysts less subject to structural transformations, and more resistant to poisons and coke formation. This is of central interest for industry.

But the direct applications of this knowledge are certainly not the only results of the investigations made in Academia and Industry. Recent trends in Catalytic Science and Chemical Reaction Engineering suggest that far reaching prospects could be expected. Progress is still slow and new ideas need time to penetrate the scientific community. Nevertheless, results already demonstrate that studies in catalyst deactivation play a major role in the identification of the real catalytic system in particular the structure and texture of the solid, which is often in a metastable state, as it is operated in the industrial reactor. These studies also allow identifying the experimental conditions which preserve this active and selective state. This is crucial for a real understanding of catalysts and catalysis. Another area of catalytic science concerns reactions kinetics, which, if properly determined, are of a paramount importance in the elucidation of mechanisms. The behavior of the kinetics during aging and deactivation and an accurate modeling of the evolution of activity and selectivity are essential information for the process performance. These are just two typical examples, but quite generally, although progress is still timid, the science of catalyst deactivation is going to be more oriented to fundamental issues.

The reader of the Proceedings of Catalyst Deactivation 1999 will find lectures and contributions dealing with many aspects of catalyst deactivation or characterization of deactivated catalysts. Some case studies illustrate both the complexity and the investigations to be conducted and the benefit of a better understanding.

We are very happy of the international character of this symposium : the contributions originated from 21 countries. We are confident that the discussions during the Symposium itself and these Proceedings will contribute to the development of this field of research and will promote a further increase of fruitful contacts between academic and industrial investigators.

**B.Delmon
G.F.Froment**

Chairmen

PREFACE

The 8th International Symposium on Catalyst Deactivation, 1999, was organized by:
The Technological Institute of the Royal Flemish Society of Engineers (TI - K VIV)

The K VIV is the professional organization of the academically trained Flemish engineers. It represents more than 11.000 members.

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KEYNOTE LECTURES

Coping with Catalyst Deactivation in Hydrocarbon Processing

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Summary

Coping with catalyst deactivation and poisoning is a continuous challenge in hydrocarbon processing. Innovation of the processes in an integrated manner, which encompasses catalysts, process line-ups, process conditions and reactors, has provided the required break-throughs and will continue to do so in the future. Several examples are given, gas oil hydrotreating, vacuum gas oil (mild) hydrocracking, residue hydroprocessing, atmospheric residue FCC and naphtha reforming.

1. Introduction

In a modern refinery a large number of conversion processes transform crude oil into valuable transportation fuels such as gasoline, kerosene and diesel, and intermediates for the petrochemical

industry [1,2]. In all the catalytic conversion and treating processes catalyst deactivation, for instance by coke deposition, precipitation of metal sulfides and poisoning, plays an important role, see Figure 1. Coping with deactivation and poisoning is a continuous challenge for industrial researchers, in particular in the light of increasingly tight product specifications. Innovation of the processes via integrated innovation of reactor technologies, process line-ups and catalysts, is their answer to these challenges. This review deals with coping with deactivation in several

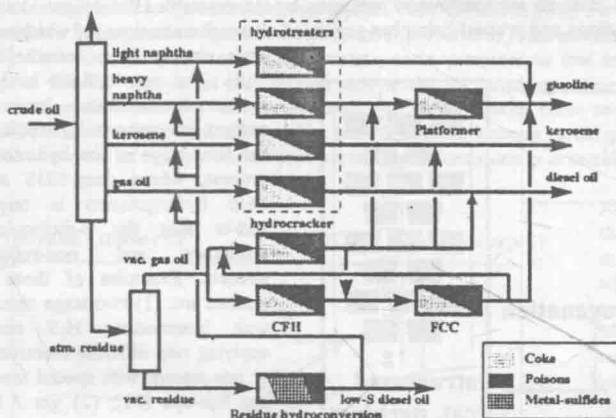


Figure 1. Coke, poisons and metal sulfides deposition in crude oil processing (Reprinted, adapted from reference [1], with kind permission from Kluwer Academic Publishers)

of the main refinery processes, hydrotreating, hydrocracking, residue hydroprocessing, catalytic cracking and catalytic reforming.

2. Hydrotreating

There are numerous ways in which hydrotreating and, more generally, hydroprocessing catalysts may deactivate: (1) covering of the active sites by reactants, products or other molecules via selective adsorption/poisoning; (2) sintering or decomposition of the active phase(s); (3) deposition of coke and/or metal sulfides [3]. Coke deactivation occurs in principle in hydrotreating of all oil fractions, see Figure 1 [3]. The heavier the oil fraction the more pronounced coke deactivation can become, but by operating at higher hydrogen pressure this is counteracted. Metals deposition occurs mainly in the hydrotreating of atmospheric and vacuum residues, see section 4. Coke deactivates the hydrotreating

catalyst both by active site coverage and by pore plugging, depending on the catalyst age. Coke accumulates on the alumina support of the hydrotreating catalysts and in this way blocks the active edges of the CoMoS-slabs [3]. The deactivation is relatively rapid in the initial phase of the catalyst due to adsorption of polynuclear aromatics and N-containing aromatics [3,4]. In general, heteroatom-containing molecules have the tendency to poison the hydrotreating catalysts by adsorbing on the active sites. Furthermore, poisoning by deposition of silica may occur when hydrotreating coker products, where silicone oil is added as anti-foaming agent [3]. Despite the importance of coke deposition, there is strong evidence (TEM, EXAFS) that the deactivation of catalysts used in VGO hydrotreating is at least partly due to a loss in MoS₂ dispersion, often with the concomitant segregation of the promoter sulfide, Ni₃S₂ or Co₉S₈ [5-8]. An important parameter in catalyst design is, therefore, to control the interaction between metal and support. During regeneration of a spent catalyst the metals should be re-dispersed, and usually are to a large extent, unless the sintering during operation has been too great [5-7].

The increasingly stringent specifications on transportation fuels still pose interesting challenges on the hydrotreating processes and its catalysts. Gas oil hydrodesulfurization and hydrogenation is a typical example in this respect [1,2,9]. To meet the new specifications on sulfur and aromatics levels in the diesel oil, refiners operating single stage gas oil hydrotreaters have several options: (1) decreasing throughput, which implies either decreasing the amount of diesel oil produced or installation of extra reactor capacity, both options being very expensive; (2) increasing the hydrogen (partial) pressure, also an expensive option; (3) improving the activity of the conventional catalysts, though step-out changes are not expected; (4) increasing temperature, which increases catalyst deactivation by coke deposition and, though beneficial for hydrodesulfurization (HDS), can negatively affect the hydrogenation because this is an equilibrium-limited reaction. Dedicated noble-metals-based hydrogenation catalysts and to a lesser extent, also the HDS catalysts are sensitive to poisoning by the inevitable HDS by-product, H₂S. Innovation in reactor technology and process lining has generated alternative solutions, of which several

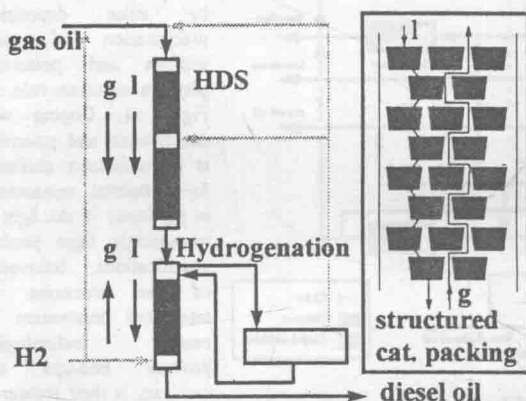


Figure 2. Decrease in the level of poisoning by H₂S in deep-HDS and deep hydrogenation of gas oil: gas/liquid counter-current operation and structured catalyst packing as future innovation [1,12,16] (Reprinted, adapted from reference [1], with kind permission from Kluwer Academic Publishers)

which is treated in gas /liquid counter-current operation [13]; (4) again a split into a light and heavy stream, but now with the heavy stream being subject to mild hydrocracking and the light stream to desulfurisation, followed by deep-hydrogenation of both streams after removal of gaseous poisons [14]. New process innovations, such as catalytic distillation [15] and full reactor gas / liquid counter-current operation applying structured catalyst packing, see Figure 2, [16] have already been reported.

have already been commercialised [1,2]. The new options have two themes in common: lower the amount of gaseous H₂S poison in the final stage of the hydrotreating process, where deep-HDS and/or deep hydrogenation is targeted, and/or split the S-molecules in refractory and non-refractory streams. Examples of these new options are: (1) two-stage operation with intermediate H₂S removal applying two different reactors [10] or one reactor with special feed and gas line-ups [11]; (2) gas / liquid counter-current operation (conventional hydrotreating is carried out in gas / liquid co-current operation), see Figure 2 [12]; (3) split of gas oil stream in a light fraction, which is treated in gas / liquid co-current operation and a heavy stream, containing the more refractory S-containing molecules,

3. Hydrocracking

The hydrocracking process is used in the refinery mainly to convert heavy gas oils and vacuum gas oils (e.g. 370-540 °C) to lighter and high quality products like naphtha (e.g. C₅-180 °C), kerosene (e.g. 180-250 °C) and diesel oil (e.g. 250-370 °C), and to deeply remove hetero-atoms. Depending on the actual design, hydrowax (e.g. 370-540 °C), an excellent feedstock for a wide variety of other processes, such as ethylene cracker, FCC, base oil manufacture, can also be produced [1,2]. When focusing on virtually metals-free feedstocks, the main reason for catalyst deactivation in hydrocracking is coke formation [17], although it has been reported that some forms of coke could also be beneficial [18]. However, coke deactivation generally determines cycle length [17,19]. Some Mo[W]S₂ sintering and release of Ni from its edges (the latter especially at low H₂S partial pressure [20]) also takes place [21,22], which affects the performance of the hydrocracking catalyst, and should be reversed during regeneration. Coke can be both formed from precursors present in the feed, for instance asphaltene-like molecules [23,24], and from (poly)-aromatic molecules formed during the process itself as result of condensation reactions [25,26]. Coke covers active sites, hinders transport of reactants and products, and eventually block pores. In principle, coke deactivation of these bifunctional catalysts results in different deactivation rates for the different functions (presumably the acidic functions to a greater extent than the hydrogenation functions [27]), which can have a significant impact on the product selectivities of the hydrocracker reactor [19]. During time on-stream the composition of the coke changes by graphitisation, resulting in an increased C/H ratio and, in principle, also the spatial arrangement and active site coverage might change [28]. Coke formation is counteracted by the hydrogenation of the coke precursors by the catalysts, thus suppressing the steady-state coke levels on the catalysts [29]. A minimum hydrogen partial pressure is required to be effective, otherwise even de-hydrogenation reactions might be accelerated [30]. Intimate contact between the hydrogenation and the cracking active sites is considered to be beneficial to suppress coke formation [29]. For modelling purposes we can consider a hydrogenation function clearing coke (precursors) from an annulus on the support around it [31]. Under severe hydrocracking conditions - under pressures as low as 30 bar and temperatures as high as 450 °C - coke is not only formed catalytically via dehydrogenation reactions, but also thermally via condensation reactions of aromatic radicals [32,33]. Under these severe conditions vapour-liquid equilibria have an important effect on the coke formation, because partial evaporation of the feed results in local increase of coke precursor concentration and consequently in increased coking.

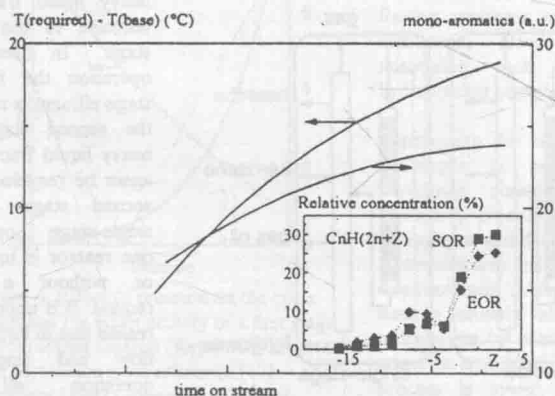


Figure 3. Effect of increasing operating temperature in single stage hydrocracking of heavy feedstocks on aromatics levels in products (Reprinted, adapted, with permission from reference [17]. Copyright (1997) American Chemical Society)

Activity-wise, deactivation of the catalyst is compensated for in commercial practice by adjusting the operating temperature (see Figure 3), whereby certain design limits cannot be exceeded, and the end-of-run temperature of the cycle is set. The start-of-run temperature is determined by the initial activity of the (fresh) catalyst. Cycle length is thus the available time-period between start- and end-of-run temperatures. In addition to activity, product selectivities and qualities also change as result of coke deactivation. This can have an impact on the cycle length: for instance, more light products may be formed than can be handled by the downstream distillation sections, or certain products

may not meet the required quality specifications as a result of the required operating temperature being too high (even if it is still below the design value), which increases the aromatics levels in the products

(see Figure 3). Fouling of equipment can also force operators to shut down the hydrocracker for maintenance and cleaning.

Cracking catalysts, containing for instance amorphous silica-alumina and/or zeolites, are sensitive to poisoning by nitrogen-containing organic molecules and, to a lesser extent, ammonia [34,35]. Therefore,

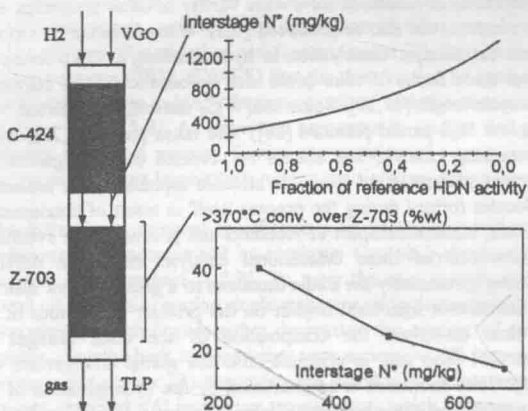


Figure 4. Poisoning of cracking catalyst in the MHC process by organic N-containing molecules [17,34] (Reprinted, adapted with permission from reference [17]. Copyright (1997) American Chemical Society.

in the first stage of the hydrocracking process generally hydrotreating catalysts are used to convert the nitrogen-containing organic molecules to ammonia (hydrodenitrogenation, HDN), while at the same time other hetero-atoms are also removed via HDS and HDO (hydrodeoxygenation). However, these first-stage hydrocracking catalysts also suffer from inhibition effects as result of the strong adsorption of the organic N-containing molecules [36]. The effect of poisoning of dedicated hydrocracking catalysts by organic N-containing molecules is clearly illustrated by the dramatic decrease in the cracking activity of a commercial hydrocracking catalyst by the increasing level of organic N-containing molecules, for instance as a result of a decrease in activity of the upstream HDN catalyst, see Figure 4,

with a C-424/Z-703 catalyst stacked bed in mild hydrocracking operation [17,34].

Several basic line-ups of the hydrocracking process have been developed [37], see Figure 5. In two-stage operation the effluent of the first and second stages are combined and sent to a fractionator for product recovery.

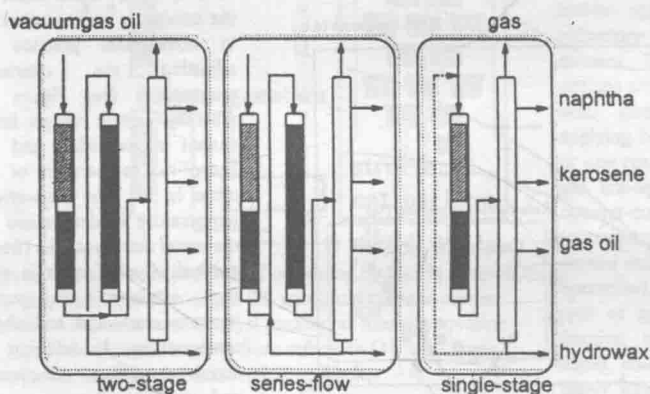


Figure 5 Different hydrocracking operation modes give different levels of poisoning [1,37] (Reprinted, adapted from reference [1] with kind permission from Kluwer Academic Publishers)

The heavy liquid fraction is recycled to the second stage. In series-flow operation the full first stage effluent is routed to the second stage. The heavy liquid fraction can again be recycled to the second stage. In the single-stage operation, one reactor is used with or without a liquid recycle. It is important to realise that in both series-flow and single-stage operation all the ammonia formed in the first stage is passed through to the second stage (or bottom of the single stage), where it poisons the dedicated

cracking catalysts. This is not the case in the two-stage operation. In addition to these fixed-bed reactor configurations, ebullating reactors (see also section 4) have also been reported for the hydrocracking process [29]. Continuous on-line catalyst withdrawal is an additional option for dealing with catalyst deactivation, see section 4 for more details.