The nanosize catalysts role in the modern hydroprocesses

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Abstract. Introduction of the modern technological procedures operating the catalytic systems with different nanosized characteristics is the only way to fabricate components of commercial oils that meet the current requirements. Specifications to the individual catalysts, which form a catalytic system, differ both in nanostructural features of the support porosity and in distribution of nanosized active site. These specifications are related to the purpose of the process and the role of the catalyst in the process.

1. Introduction
The efficiency of catalytic technologies in oil processing and oil chemistry is related to the functional properties of the catalysts such as activity, selectivity and stability. The progress in scientific understanding of the catalytic action, the use of advanced technologies and modern devices for preparing the catalysts observed in the last decade are associated with increasing demands to the quality of the products of hydroprocessing. On developing catalytic processes it is desirable not only to use the potentialities of the relevant catalysts but to control the process variables that affect their performance including hydrodynamics (the ideal displacement, the ideal mixing or an intermediate version) and kinetics (the shift of equilibrium by varying the product concentration).

2. Experimental details
In terms of the volume of the catalysts loaded in the industrial reactors of hydroprocessing, hydrodynamic characteristics of the feed stream and the mixture of gaseous products are close to a certain extent to the conditions of ideal displacement. With the aim to approach the conditions of ideal displacement, the methods and facilities are developed for a uniform (“dense”) introduction of the catalyst charge in the reactor that makes it possible to divide the downright stream of the feed stream into microstreams with the lowest transverse gradient. At the same period of time the methods and facilities are developed that serve to organize introduction of the feed stream onto the catalyst charge in the piston –bed mode: the trays of different design for the high dispersive distribution[1], “baskets” and “protective” catalysts arranged as a single layer or a number of layers. These constructions facilitate the mixing of feed to form the filter for mechanical admixtures and to trap asphaltenes and metals from heavy and recycled feeds. In some cases both the trays for high dispersive distribution and protective catalysts are used.

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However, the operation in the piston-bed mode (ideal displacement) at the inlet of the catalyst bed cannot ensure the maintenance of this mode over the entire catalyst body. When the desired reaction is accompanied by gaseous reaction products ($\text{H}_2\text{S}$ and $\text{NH}_3$ in our case) gaseous counterflows are formed, liquid flow is mixed and the role of the mixing increases. At the same time product accumulation is increasingly constrained by kinetic limitations due to the decreasing constants of equilibrium $\text{RS}+2\text{H}_2 \leftrightarrow \text{RH}_2 + \text{H}_2\text{S}$. To counterbalance the negative influence of the increasing concentrations of $\text{H}_2\text{S}$ and $\text{NH}_3$ an additional amount of hydrogen (quench) is introduced in the space between the fixed catalyst beds operated in the reactor. When a deeper desulphurization is desired the hydrogen consumption increases 5-8 times compared to that needed by the reaction chemistry [2,3;figure 1]. It is the hydrogen deficiency that limits the yield of products with the lowest sulfur content at the units currently operated for hydrotreating crude oil fractions.

![Figure 1](image_url)

**Figure 1.** The influence of the process parameters on the conversion of the sulphur in diesel fraction with industrial plant on the catalysts RK-242+RK-231Co Company Catachem ltd. («$K$» is ratio of hydrogen expense to chemical consumption)

3. Results and discussions
Catalytic distillation, that becomes increasingly important last time, integrates reaction and separation into liquid and gaseous products in a single vessel (reactor/column) charged with the fixed catalyst bed[4]. In this case, the expense of excessive hydrogen is negligible. However under these conditions the level of hydrodesulfurization is relatively small and the manufacture of the product with the lowest sulfur content requires a second stage of the process in the presence of a very efficient catalyst in excess hydrogen. Note that the excess is related to low sulfur content in the feed processed at the second stage.
Hydroprocessing in reactors with the fixed catalyst bed can also be intensified by mixing the gas–containing hydrogen, the feed and a fraction of the product (isotherming) [5]. In this case, the level of hydrodesulfurization is also relatively small and a second step including a very efficient catalyst in excess hydrogen is needed but to base content of the sulphur in this stage. However total hydrogen expense is lower than in the one-stage process.

Currently, a widespread technique is the control of the process along the height of the reactor using catalyst layers endowed with different functional properties. The layers are separated through the cavities in which the feed stream is mixed in the vicinity of the next layer. Facilities for an additional dosage of hydrogen are also installed. The catalysts are expected to meet severe requirements of high conversions at high flow rates. This can be ensured by combining a high initial activity of the nanosized active sites with their high density on the catalyst surface and the negligible influence of the diffusion that can be achieved by the trend to use the extrudates with the lowest diameter (0.8-1.2mm). The latter condition means severe requirements of the mechanical strength of the extrudates needed to maintain the integrity when subjected to overloads. When this scheme is implemented the hydrogen consumption increases many times compared to that needed by the reaction chemistry.

The transfer to two-stage processes such as catalytic distillation or isotherming considerably changes the requirements to the catalysts operating at different steps. From the catalyst for the first-stage of hydroprocessing (hydrotreatment) the highest level of conversion of sulfur containing compounds like mercaptanes, sulfides and disulfides is expected that would approache the complete conversion. The feed for the second stage includes sulfur containing compounds like thiophene and benzothiophene homologues, as well as nitrogen– containing compounds competing with sulfur containing compounds for the active sites on the catalyst surface. Accordingly, the requirements to the catalysts can be formulated.

At the first stage, the residual sulfur content in the diesel fraction cannot exceed 0.2 weight % at a high space velocity ranging from 4 to 5 h\(^{-1}\). These requirements are as a rule fulfilled by nearly each catalytic system used in one-stage processes free of hydrogen deficiency. When a two-stage operation is realized, the demands to the first-stage catalyst operated in the mode of catalytic distillation are complemented by the need to optimize the pore nanostructure.

4.Conclusions
To the catalyst used at the second step of hydroprocessing of diesel oil, a need to ensure the lowest residual sulfur content (\(\leq 10\) ppm) at a reasonable space velocity (1-2h\(^{-1}\)) is complemented by additional requirements. Among these is either high density of active sites responsible for hydrogenolysis of sulfur -containing and nitrogen -containing compounds or the presence of sites of different nature active in the hydrogenolysis of S- and N- containing compounds. The latter demand can be met either by a nanostructural design of the support or by specific conditions of introducing active components. A control of the combination of active sites on the catalyst surface is also possible through the periodical introduction of a special reagent to suppress excessive active sites.

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