



# The physico-chemical structure and activity of hydrodesulphurization catalysts aged by accelerated method



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## ABSTRACT

The research was focused on the verification of the accelerated testing method for the testing of long term catalytic activity. The verification was carried out with two types (CoMo/Al<sub>2</sub>O<sub>3</sub> and NiW/Al<sub>2</sub>O<sub>3</sub>) of commercial HDS catalysts. The catalysts were also placed into the industrial reactor and allowed to run for approximately 16 months under the industrial conditions. Then the residual activity of the catalysts was determined. The results from the accelerated and the industrial deactivation were compared.

The accelerated method included (i) the testing of the initial activity and (ii) the determination of decreasing rate of activity. The deactivation step was implemented by the injection of highly aromatic raw materials with a coking tendency. After the deactivation period the typical conditions were set (pressure 4.5 MPa, hydrogen flow 300 Nm<sup>3</sup>/m<sup>3</sup>, and WHSV 1.0 kg/dm<sup>3</sup><sub>cat</sub>). Subsequently, the reaction temperature for sulfur level 10 ppmw was determined.

The implementation of accelerated method was assessed by evaluation of physical and chemical composition of the aged catalysts. The effect of coking and active phase changes on the deactivation was also described. Raman spectroscopy and SEM-EDS analyses were realized for characterization of coke deposited in the aged catalysts.

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## 1. Introduction

The hydrodesulphurization (HDS) of motor fuel components is one of the important refining processes. Often it is supported by laboratory-scale testing facilities with a big benefit. Laboratory trickle bed reactors are frequently used for the prediction of catalyst performance, especially for the verification of catalyst activity under specific conditions. They allow using of there all feedstock and operating conditions for a particular unit, before the catalyst is loaded into the industrial unit [1].

HDS catalysts are the most important industrial catalysts. Their activity significantly affects the quality of the diesel fuel and any inappropriate choice would have a negative impact on the economy of diesel production [1–3]. The successful industrial catalytic system is dependent on data obtained in the laboratory scale. They help to predict the behavior of the processing unit. Therefore, the proper procedure of HDS catalyst testing has a big importance. The HDS process is over 70 years old but it is still subject of continuing changes. Over the years refineries have been processing heavier

and more complicated feeds due to the shifting of crude oil diversity and sources.

The significant progress has been achieved in the development of new HDS catalysts in the recent years. The intensive effort of catalyst scientists worldwide has been devoted to the development of highly active hydrotreating catalysts for the deep desulphurization of diesel fractions to ultra-low sulphur levels. The catalysts with very high HDS activity are being continuously developed and introduced to the market by the major catalyst producers [4–6]. The development of the improved HDS catalysts has been possible through the clear understanding of the key properties, namely, the nature of the active sites and their structure, the influence of a support and the textural characteristics of supports that have significant influence on the catalyst performance [7]. The continuously increasing demand for the high performance HDS catalysts is the result of tighter environmental requirements. In the recent years, the HDS catalyst has been optimized for the specific reaction conditions and the characteristics of the processed feed material. The catalysts are often tailor made for the given refinery and its local conditions to minimize its diesel production costs [8]. The research and development of the new catalysts increases the importance of testing for catalyst producers to verify catalytic activity and other properties.

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Frequently, only the initial catalytic activity is tested. The result of the initial catalyst activity informs how the catalyst will perform during the first weeks of an operation [9,10]. However, the initial activity does not express how long the catalyst could be operated under the specific conditions in a given industrial unit. The catalysts, mostly based on Ni, Co, Mo and W sulphides, are susceptible to several deactivation mechanisms during their life cycle. The deactivation is going to be more critical due to the ongoing trend in increasing HDS severity and maximizing the catalyst performance. The deactivation of the catalyst is attributed to the three main causes: (i) the coke deposition (including both—the pore plugging and the catalytic site blocking), (ii) the metals deposition and (iii) the segregation of the active phase.

In the industrial units the catalyst deactivation is compensated by temperature increase to the maximum permissible end-of-run (EOR) to maintain the catalyst performance [11,12]. Deactivation rate is different for each catalyst and depends on several factors, such as process parameters, feedstock source and its quality. Hydrotreating reactors are usually operated under a constant performance to achieve the desired product specifications. The determination of the long term activity of HDS catalysts is not often applied to incorporate time constraints and economic factors. The HDS catalysts are so stable, that the change of their activity in a laboratory scale reactor is not observed during the length of a test for about 1–2 month [13]. Hence our research is focused on the creating of a new accelerated methodology which can be used for the prediction of the long term activity during the test length of about 14 days.

## 2. Experimental

The accelerated methodology involved (i) the determination of the initial activity at standard conditions, (ii) the deactivation step and (iii) the testing of the residual activity at the standard conditions. The initial and residual activity was used for the calculation of the deactivation rate and for prediction of the specific catalyst operation period length under the conditions of the given industrial unit.

The developed method was completed by the detailed characterization of the aged catalysts. The basic kinetic parameters were calculated too.

### 2.1. Catalyst loading into a pilot plant reactor

The testing reactor was loaded with 100 mL of a catalyst. The accelerated methodology was verified on two types of commercial catalysts based on (1) CoMo/Al<sub>2</sub>O<sub>3</sub>, (2) NiW/Al<sub>2</sub>O<sub>3</sub>. The catalysts were tested in their original form. Before loading into the reactor the catalyst was diluted 1:1 volumetric with an inert (silicon carbide SiC, size 0.1 mm, MESH 80) to ensure the proper hydrodynamic conditions over the catalytic bed. SiC (size 1–2 mm, MESH 12) was placed into the reactor below and on the top of the catalyst bed too. SiC in the lower part of the reactor (i.e. below the catalyst bed) fixed the catalyst bed in the isothermal zone of the reactor. SiC in the upper part of the reactor (i.e. above the catalyst bed) ensured the preheating and proper mixing of the feedstock and hydrogen before the entering the catalyst bed. The catalyst activation or transform of inactive oxides to active sulphides form was realized inside the trickle bed reactor. A standard catalyst activation procedure using atmospheric gas oil (AGO) with dimethyl disulfide (DMDS) was used. The activation procedure consists from several steps. (1) – The reactor was heated up to 120 °C (rate 20 °C/h) under nitrogen flow rate. After reaching target temperature (120 °C) the gas flow from nitrogen to hydrogen was switched and at the same time the injection of sulphidation feedstock (AGO + 3% DMDS) was started.

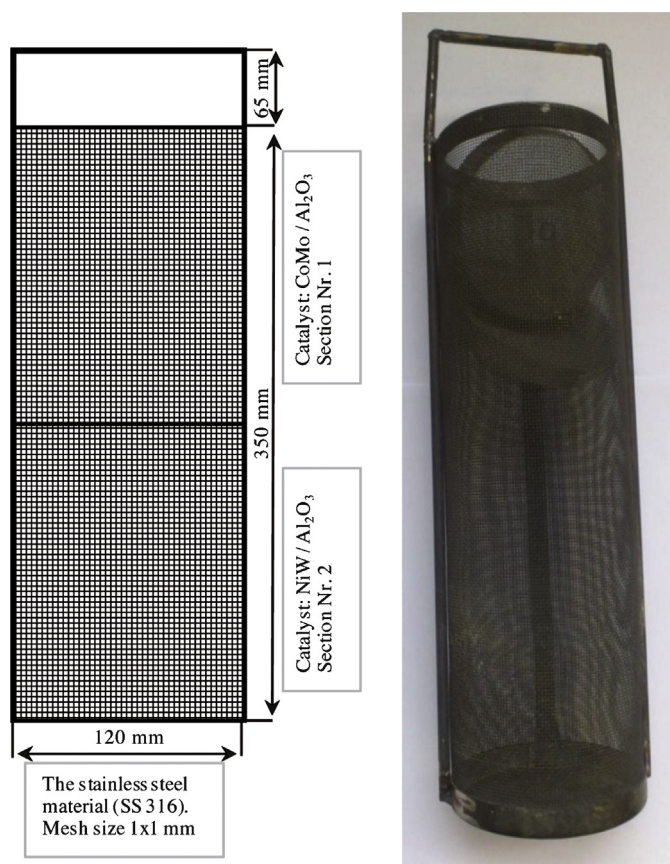


Fig. 1. The scheme of used cylindrical basket for industrial catalyst deactivation.

(2) – The reactor was heated up to 220 °C (rate 10 °C/h). At temperature 220 °C was first stabilization period, about 10 h. After stabilization period, the reactor was heated up to 280 °C (rate 10 °C/h). At 280 °C was second stabilization period, about 10 h. The last step was increasing of temperature up to 360 °C still with feeding AGO + 3% DMDS. At the temperature 360 °C was finished activation process.

### 2.2. Catalyst in an industrial reactor

The catalysts were also deactivated in the industrial reactor. The catalysts were placed in a special SS316 cylindrical basket with 120 mm of inner diameter and 350 mm length. The scheme and photo of the basket can be seen in Fig. 1. The half of the basket was filled with NiW/Al<sub>2</sub>O<sub>3</sub> commercial catalyst and the second half with the catalyst based on CoMo/Al<sub>2</sub>O<sub>3</sub>. The special basket filled with both HDS catalysts was loaded into the upper part of catalytic layer of industrial reactor.

### 2.3. Analyses of feeds and products

The basic properties of the feeds and products were determined: (i) density (densitometer DA 645 KYOTO ELECTRONICS, ASTM D4052); (ii) refractive index (RFM 970, Bellingham-Stanley Ltd., ASTM D1218); (iii) color (Lovibond PFX880, ASTM D1500).

The content of sulfur was assessed according to ASTM D3120 by oxidative micro-coulometry using Thermo Euroglass ESC 1200. The nitrogen content was determined using Total Nitrogen Analyser TN-100 (ASTM D4629). The content of aromatics was investigated by the multidimensional chromatographic method (GC×GC). The chromatograph was equipped with a cryo-modulator and the secondary oven with a polar column (VF-WAXms 20 × 0.1 × 0.1). The different types of hydrocarbons were separated in the primary

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