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Supported on alumina Co-Mo hydrotreating catalysts: Dependence of catalytic and strength characteristics on the initial AlOOH particle morphology

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ABSTRACT

The influence of different initial AlOOH boehmites on the mechanical strength, textural characteristics, and activity of diesel fuel hydrotreating catalysts has been studied. The morphology of the initial AlOOH particles was shown to have no significant influence on the composition and structure of the Co-Mo-S phase, although it does fully define the mechanical strength and textural characteristics of the catalysts. An optimal combination of high mechanical strength and catalytic activity, which depends on a texture of the catalyst, is attained using initial boehmite with a needle-shaped particle morphology and a particle size of 150 nm × 8 nm × 8 nm.

1. Introduction

Currently, most diesel fuels with ultra-low sulphur content (ULSD) are produced in industry using supported Co(Ni)-Mo/Al_2O_3 catalysts [1]. Modern catalysts generally contain supported metals in the form of highly active and fully sulphided bimetallic compounds with little interaction with the support. This active component is often called Co(Ni)-Mo-S phase of Type II [1–5]. The selective synthesis of Co(Ni)-Mo-S phase of Type II has been sufficiently developed in industry, as confirmed by the presence of this phase in different industrial catalysts [3]. The basic steps of the preparation of catalysts that are suitable for industrial application and preferentially contain Co(Ni)-Mo-S phase of Type II are the selection of supports modified with compounds that minimise chemical interactions between the support and active metals, the addition of chelating organic compounds into the impregnating solutions, the drying of catalysts at low temperatures, and the application of specific sulphidation techniques [1–8]. Thus, a general approach to the synthesis of the supported high-activity sulphided compound is defined and can be modified to achieve particular goals, such as the preparation of hydrotreating catalysts fora specific type of fuel.

However, the situation for catalyst supports is more complicated. The industry advanced a set of new requirements for catalysts that are fully defined by the characteristics of the supports used. Ideally, supports provide the optimal textural characteristics for the catalyst in combination with high mechanical strength at minimal granule cross-section. The main textural characteristics are average surface area, pore volume, and pore size distribution. High-activity catalysts for the production of ULSD generally contain 10–15% of Mo and 3–5% of Co(Ni), e.g., [8,9]. The optimal surface metal concentration is 2–3 Co(Ni) atoms and 5–8 Mo atoms per nm^2 [3],which is more than a monolayer filling of the surface by Co(Ni)-Mo-S or molybdenum oxide [10]. Accordingly, the average surface area of the catalysts is 150–200 m^2/g. The average surface area of a catalyst depends on the average pore diameter, which is in turn defined by the sulphur-containing molecules of the feed. To achieve maximum conversion of the largest and least reactive sulphur compounds in diesel fuels, namely, homologs of dibenzothiophene with several alkyl groups [1,11,12], they must be able to access the active component particles. Thus, a hydrotreating catalyst of middle distillates should contain pores with the diameters of

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70–180 Å [13] and major part of these pores should have diameters in the range of 70–130 Å [14].

The pore volume of a catalyst should be not less than 0.4 cm^3/g to provide the active component with access to the feed and to localise the inevitably formed carbon deposits. Catalysts with a pore volume of more than 0.6 cm^3/g should not be used because this pore volume decreases the active component concentration per unit volume of the reactor. Thus, an average surface area of 150–200 m^2/g, a pore volume of 0.4–0.6 cm^3/g, and an average pore diameter of 10.0 ± 3.0 nm are optimal for catalysts used in the deep hydrotreatment of diesel fuels. We arrived at these conclusions based on a large amount of modern industrial catalysts. Similar conclusions were made by Eijsbouts in the review [14].

The supporting 10–15% Mo and 3–5% Co(Ni) using different methods results in the decrease in an average surface area of 50 ± 10 m^2/g, a pore volume of 0.20 ± 0.05 cm^3/g and an average pore diameter of 0.5–1.0 nm, e.g., [6,9,10,14,15]. To compensate for the deterioration of textural characteristics due to the deposition of Mo, Co, or Ni compounds on the surface, an initial support should have an average surface area of 200–250 m^2/g, an average pore diameter of no less than 9.0 nm, and a pore volume of 0.6–0.8 cm^3/g.

Industrial hydrotreating process of middle distillates is usually performed in trickle-bed reactors with parallel top-down supply of feedstock and hydrogen [16,17]. Portion of diesel fuel passes through the reactor as a liquid and forms channels in a catalyst bed. Large bed height could lead to non-uniform liquid flow along granules and portion of granule surface will remain dry [17]. To provide optimal mass transfer through the catalyst bed and diffusion of the feed along the catalyst granule, it is necessary to use granules with minimal volume-to-surface ratio and minimal granule diameter. However, granules could not have sizes less than 1 mm because it leads to significant pressure drop in the reactor [17]. Consequently, catalyst granules with trilobe and quadrilobe cross-section and the diameters of 1.0–1.5 mm are the most effective for deep hydrotreatment, while cylindrical granules with the diameters of more than 2 mm were used previously [14,16–21].

To provide an optimal diffusion of the feed along the catalyst granule, granules with a minimal volume-to-surface ratio and minimal granule diameter should be used. In addition, granules in the form of trilobe or quadrilobe extrudates with a cross-section diameter less than 1.5 mm are the most effective in hydrotreating [14,16–19]. However, the smaller the granule, the lower its mechanical strength is. In recent years, the bed volume of a catalyst has had to be increased by more than three-fold [12] because of the conversion to the production of ULSD while preserving the general productivity of industrial units. Accordingly, requirements for the mechanical strength of catalysts have increased. Previously, ASTM D4179-88a (Standard Test Method for Single Pellet Crush Strength of Formed Catalyst Spheres) and ASTM D6175-98 (Standard Test Method for Radial Crush Strength of Extruded Catalyst Particles) had been widely used to define the mechanical strength of hydrotreating catalysts. These methods are based on strength measurements of single, well-selected granules with no defects and deformations. Consequently, these methods do not always provide accurate values for real catalysts, especially catalysts in the form of extrudates with complex cross-sections and small sizes, which comprise nearly all modern catalysts for ULSD production.

For the catalysts, which are loaded into the reactor as a dense bed, mechanical strength is defined using the amount of dust formed. Dust formation is caused by the destruction of granules during mechanical impact on the bed. The more dust formed, the greater the pressure drop along the reactor is [20,22]. Consequently, for hydrotreating catalysts, methods based on the determination of a mechanical strength for a large volume of a catalyst are more appropriate than those for a single granule. Some methods for determining bulk crushing strength and their advantages over techniques for strength measurements of single granules are described in [22,23]. Currently, industrial plants require the bulk crushing strength of hydrotreating catalysts to be not less than 1.5 MPa according to the Shell SMS 1471 or ASTM 7084-4 methods. The strength of a catalyst depends on many factors, such as the impregnation, drying [24], calcination [25], and sulphidation conditions [26]. However, the strength of initial supports has the greatest influence on the final catalyst strength.

Thus, the strength and textural characteristics of catalysts, which have significant influence on catalytic properties, are largely defined by the strength and texture of the initial supports, namely, extrudates of alumina oxide. Different results can be obtained using the same initial pseudoboehmite subjected to various natures and concentrations of peptising agents, paste wetness, mixture conditions, granulations, and drying and calcination conditions [14,24–27]. To produce granulated γ-Al_2O_3, initial pseudoboehmite is often peptised using nitric acid in the mixer with Z-folded beaters and extruded using a spinneret from polymeric material at 1.0–3.0 MPa. Next, wet extrudates are dried at a temperature slightly higher than 100 °C and calcined at 550 °C. An increase in the HNO_3/AlOOH ratio leads to an increase in the mechanical strength and decrease in the volume and average pore diameter [14,28,29], and a typical HNO_3/Al_2O_3 mole ratio in paste is in the range of 0.03–0.05 [29]. Thus, the conditions used in the industrial preparation of γ-Al_2O_3 extrudates are similar, with the texture and strength of initial supports being generally defined by the properties of the initial pseudoboehmite. If the chemical and phase composition of the initial AlOOH powders used for granulation are similar, the properties of γ-Al_2O_3 will mostly depend on the morphology of the initial boehmite or pseudoboehmite crystals.

In this study, the influence of the crystalline particle morphology of the industrial AlOOH powders on the strength, texture, and catalytic properties of Co-Mo/Al_2O_3 catalysts for the deep hydrotreatment of diesel fuels was studied.

2. Experimental

2.1. Initial powders and preparation of supports

The industrial AlOOH powders were Pural SB, TH-60, TH-80, TM-50, and TM-70, produced by Sasol, Germany, synthesised using alcoholate technology; boehmite produced by "Chimtek-Engineering", Chelyabinsk, Russia, synthesised using precipitation technology; and two boehmites produced by ISCZC, Ishimbay, Russia, synthesised using the thermochemical activation of gibbsite followed by plasticisation in autoclave with nitric acid and spray drying [30] under different plasticisation conditions and designated as ISCZC-1 and ISCZC-2. The main characteristics of the powders are shown in Table 1.

All the supports were synthesised using the same method. Pastes with a mass ratio of $AlOOH/H_2O/HNO_3 = 1/0.7–0.8/0.014$ (HNO_3/Al_2O_3 mole ratio = 0.03) were prepared in a Z blade sigma mixer for 1 h. These ratios were specifically chosen based on a large amount of experimental data. Therefore, they were well suited for each powder. These ratios provide production of granules with specified shape and the highest mechanical strength. Increase of water amount results in a drastic decrease of mechanical strength and adhesion of granules. In addition, excess water removes during extrusion. In the case of deviation from specified parameters extrudable pastes could not be obtained.

The paste obtained was extruded using a fluoroplastic spinneret with trilobe holes on the VINCI extruder at $P = 3.5–4.0$ MPa and with the plunger moving at 1.2 mm/s. Extrudates were dried for 4 h at 120 °C in air flow, then heated to 550 °C for 2 h and calcined at