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## Using the Mechanical Activation for Obtaining the Sulphide Catalysts of Hydrogenolysis

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### Abstract

For the first time, an approach to a single-stage manufacture of bulky sulphide catalysts using a solid-phase method performed by means of the mechanical activation of a mixture consisting of coarse molybdenum disulphide and cobalt powders, in the presence of detonation nanodiamonds is described. An effect exerted by the mechanical treatment duration, ratio between the initial components and nanodiamonds on the process of nanofragmentation of molybdenum disulphide and activity of catalytic systems obtained in the model reaction of DBT hydrodesulphurisation has been studied.

**Key words:** mechanical activation, hydrorefining, sulphide catalysts, model reaction, hydrodesulphurisation of dibenzothiophene

### INTRODUCTION

According to Russian scientists, the problem of the selective synthesis of an active component in supported catalytic systems for the hydrorefining of petroleum fractions is currently solved [1]. The continuation of research work in this field is associated with improving the application and sulphidation technologies for the active components, the optimization of chemical and phase composition, textural, grain-size and strength characteristics of the carrier proper.

The further development of the catalysts for hydrogenolysis, both in Russia and abroad, is associated with the development of new methods and technologies for producing bulk catalysts. They differ favourably from the supported catalyst systems in the fact that they allow freely varying the concentration of the

active component and eliminating the use of aqueous reagent solutions.

Currently, fundamentally new methods for preparing the Ni-(Co)-Mo(W)-S compositions, containing no carriers are under development. They are based on the synthesis of nanostructures by means of the coprecipitation of the precursors of active components [2], via mechanochemical combination either of nickel and molybdenum precursor salts, or of micron size Ni, W, Mo, Al powders with further leaching. For this purpose, researchers use also ammonium tetrathiomolybdate  $(\text{NH}_4)_2\text{MoS}_4$  high temperature decomposition as well as the synthesis of nanosized heterogeneous catalyst precursor particles in the micellar three-phased system such as reverse microemulsion solution  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ /surfactant/pentadecane [3–6]. Earlier we synthesized sulphide catalysts from

metal nanopowders in a single stage [7] *via* direct sulphidizing the nanopowders of molybdenum, cobalt, nickel. Later we performed the synthesis *via* a mechanical combination of coarse commercial molybdenum disulphide, and the nanopowders of 3s metals [8]. However, these catalytic systems provide an insufficient level of hydrodesulphurization being an order of magnitude worse in the activity than modern industrial hydrorefining catalysts ( $S_{\text{res}} \approx 0.001$  mass %).

This work continues the experimental search started earlier for a simple and environmentally friendly method of synthesizing sulphide catalysts for hydrorefining fuel oil fractions. The purpose of the work consisted in obtaining bulky sulphide catalyst *via* a solid phase method in a single stage by means of a mechano chemical combination of coarse molybdenum disulphide and cobalt powders in the presence of detonation nanodiamonds, as well as in studying the activity of the catalyst systems obtained.

Nanodiamonds were used as a third component, firstly, in order to provide dispersing the coarse powders of cobalt and molybdenum disulphide, and secondly, taking into account the information concerning the catalytic activity of nanodiamonds in the reactions of isomerisation, dehydrogenation, disproportionation and polycondensation [9].

## EXPERIMENTAL

As starting materials for the synthesis of the catalyst systems, we used: commercial coarse molybdenum disulphide powders ( $\text{MoS}_2$ , DMI-7, derived from mineral molybdenite, the main substance content amounting to 99.72 %), cobalt (PK-1U grade, obtained *via* electrical method for the purposes of powder metallurgy and obtaining magnets, average particle size amounting to 70  $\mu\text{m}$  State Standard GOST 9721-79), as well as detonation nanodiamonds (ND, serial, supplier the SKN Co. Ltd., Snezhinsk City (Russia); synthesis of the material from a TG-50 grade graphite in the ice shell, cleaning *via* acid-chromium method, the mass fraction of unburned residue being less than 2.0 %, the average primary particle size being of 4 nm).

The synthesis of catalysts with ratio values  $\text{Co}/\text{ND}/\text{MoS}_2 = 1 : 3 : 3$  and  $1 : 1 : 5$  was per-

formed *via* the mechanical treatment of the components in a vertical vibratory mill under vacuum ( $10^{-5}$  Torr) at a frequency of 16 Hz, amplitude 2 mm, and the duration of mechanoactivation equal to 0.5–8 h. The product obtained was stored in an inert atmosphere of argon. Electron micrographs were obtained using a Philips CM-30 electron microscope. The activity of the catalysts was evaluated according to the residual sulphur content occurred in the course of hydrodesulphurising a model compound (dibenzothiophene, DBT, analytical wavelength  $\lambda = 324$  nm) and to the corresponding values of DBT conversion rate constants. The experiments were performed using a closed-type reactor with the overall capacity of 100 ml, at a pressure of 3.0 MPa at a temperature of 340 °C. The catalyst download was 0.64 g that of the model mixture was 62 g (80 mL). The initial concentration of DBT solution in hexadecane was equal to 0.05 % for sulphur. Rate constants of hydrogenolysis of DBT ( $k$ ) were found assuming the pseudo-first order of DBT conversion:

$$C_{\text{DBT}} = C_{\text{DBT}}^0 e^{-kt} \quad (1)$$

where  $C_{\text{DBT}}^0$  and  $C_{\text{DBT}}$  are the initial and final content of DBT in hexadecane solution, respectively;  $k$  is the slope of the straight line;  $t$  is time.

After converting the rate expression takes the form

$$\ln\left(\frac{C_{\text{DBT}}^0}{C_{\text{DBT}}}\right) = kt \quad (2)$$

We obtained corresponding values rate constants ( $k$ ) of the tangent of the angle of

the slope of the dependency  $\ln\left(\frac{C_{\text{DBT}}^0}{C_{\text{DBT}}}\right)$

from  $t$ . The samples were sequentially taken from the reactor (volume 0.5 mL aliquots) in 0.5, 1, 2, 3, 4, 6 and 7 h. The elemental sulphur content in the final samples was determined using an X-ray fluorescence technique (sulphur analyzer OXFORD Instruments Lab-X 3500 SCL). Changing the concentration of DBT in the intermediate samples was determined by means of spectrophotometry (Uvikon-943, Kontron Instruments, Italy) at the analytical wavelength  $\lambda = 324$  nm. The activity of the

catalyst systems obtained was compared with a domestic supported catalyst.

## RESULTS AND DISCUSSION

Molybdenum disulphide crystals have a shape of hexagonal platelets that are split perpendicular to the main axis to give very thin petals. In the crystal lattice of  $\text{MoS}_2$  each molybdenum atom is located at the centre of the six sulphur atoms located at the corners of a triangular prism [10]. For supported sulphide catalysts, the issues of manifesting the mechanisms of the activity thereof are investigated profoundly enough. Today, one consider indisputable the fact that the active phase in the supported catalysts represents molybdenum disulphide nanocrystallites with the size 3–5 nm having a stack structure with the number of crystallites in the stack amounting to 1–2, those are weakly bound chemically with the carrier [11].

The catalysts were prepared from three components at different ratio between them and at different duration of mechanical activation (MA).

The photomicrograph of molybdenum disulphide (Fig. 1) demonstrates the interplanar spacing between crystal faces to amount to 0.61 nm, which is inherent in  $\text{MoS}_2$ . In the course of the mechanical dispersing the system of  $\text{Co}/\text{ND}/\text{MoS}_2 = 1 : 3 : 3$  within the duration range of 0.5–8.0 h, there occurs the nanofragmentation of  $\text{MoS}_2$  large crystals to form nanocrystallites (Figs. 2 and 3) with a “curved” configura-

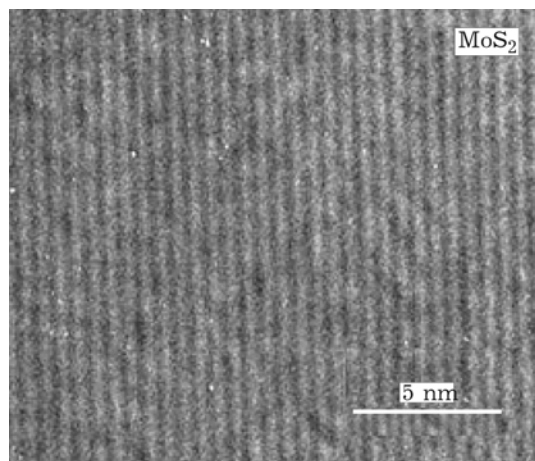


Fig. 1. Photomicrograph of the initial  $\text{MoS}_2$ .

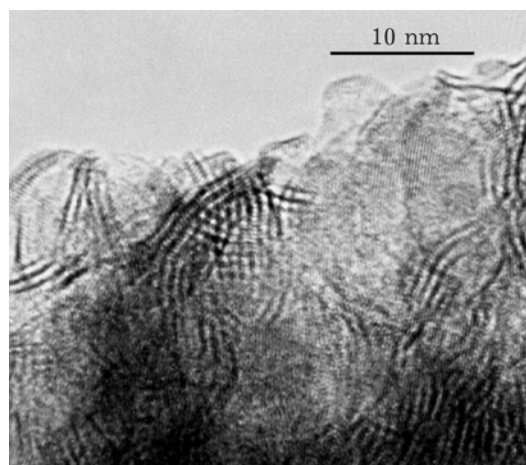


Fig. 2. Electron microscopy image of catalyst II (MA duration 4 h).

tion. According to the authors of [5], in case of the model reactions of alkene hydrogenation, isomerization and deuterium exchange, the level of catalytic activity of  $\text{MoS}_2$  obtained *via* ammonium thiomolybdate thermal decomposition, correlate with the bending level of nanosized lamellar nanoscale crystals associated into the packages. The nanodiamonds themselves are exhibited as “spots” with the interplanar distance between the faces of crystals equal to 0.2 nm. The particles of cobalt on electronic images could not recognize. According to Figs. 2 and 3, under the conditions of mechanical activation, the formation of larger molybdenum disulphide nanocrystallites is observed comparing to those being a part of the active phase in supported catalysts [12].

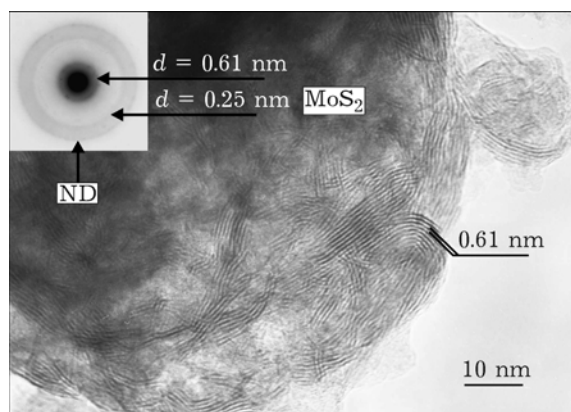


Fig. 3. Photomicrograph of catalyst II (MA duration 8 h).

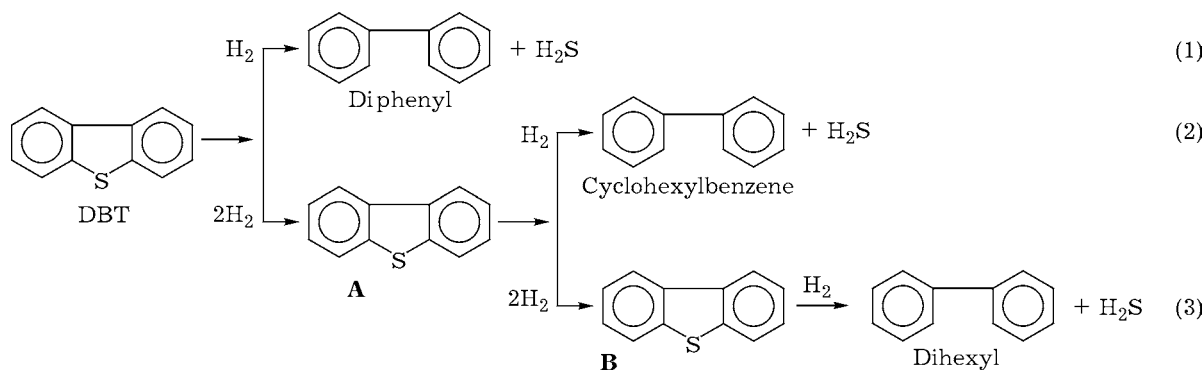


Fig. 4 Scheme of dibenzothiophene (DBT) hydrodesulphurization, and possible reaction products.

In order to assess the activity of the catalysts with respect to compounds belonging to the dibenzothiophene series those are present in the diesel fractions, being included in the group of compounds most resistant to hydrorefining, researchers traditionally use DBT hydrodesulphurisation as a model reaction. The sequence of the reactions in the course of DBT hydrodesulphurisation is presented in Fig. 4.

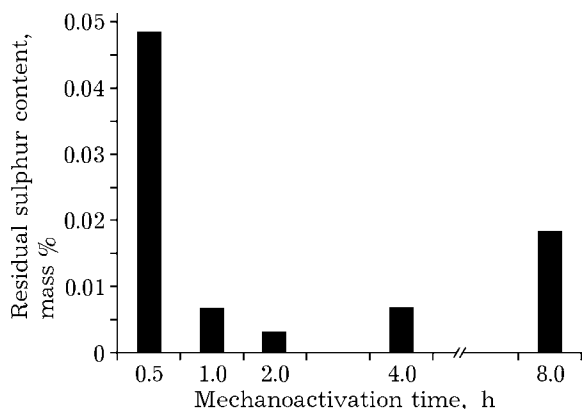


Fig. 5. Effect of MA duration on the residual sulphur content in the presence of catalyst I.

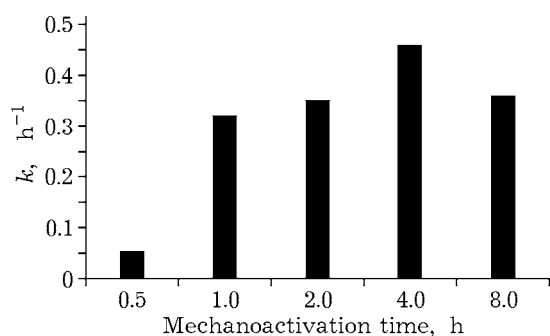


Fig. 6. Effect of MA duration on the DBT hydrogenolysis rate constant ( $k$ ) in the presence of catalyst I.

The activity of catalytic systems in the model reaction was determined for two series of catalysts (I and II), characterized by the composition ( $Co/HA/MoS_2 = 1:1:5$  and  $1:3:3$ , respectively) and the time of MA. The catalysts were prepared under the conditions of different duration in the joint mechanical treatment of the starting components amounting to 0.5, 1, 2, 4 and 8 h. The activity of the catalyst systems was assessed basing on the residual sulphur content in the reaction mixture after 7 h and on the hydrodesulphurization rate constant for the model compound.

The mechanical treatment time depends non-monotonically on the residual sulphur content in the hydrodesulphurised substance for the catalyst I (Fig. 5) and passes through a minimum that corresponds to the time of MA of 2 h. For this time of MA  $S_{res} = 0.003$  mass %,  $k = 0.35 h^{-1}$  (Fig. 6). The rate constants of DBT hy-

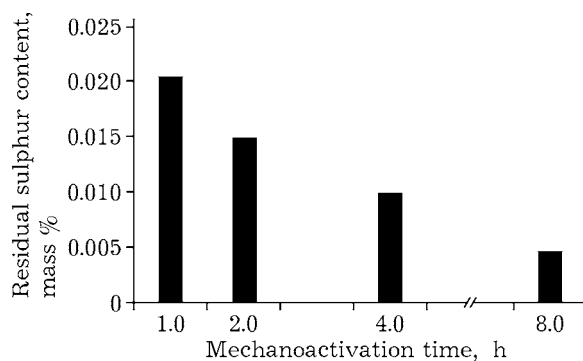


Fig. 7. Effect of MA duration on the residual sulphur content in the presence of catalyst II.

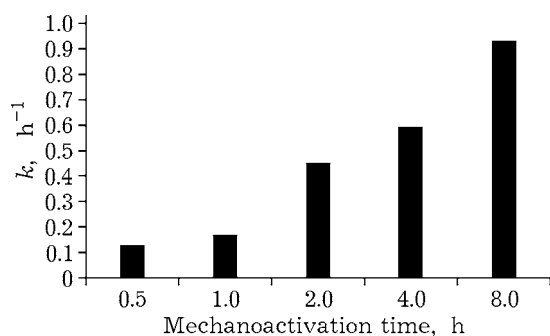


Fig. 8. Effect of MA duration on the DBT hydrogenolysis rate constant ( $k$ ) in the presence of catalyst II.

drogenolysis for MA duration equal to 4 h were slightly higher ( $k = 0.47 \text{ h}^{-1}$ ) (see Fig. 6).

In contrast to the series I catalysts, the series II catalysts exhibited the residual sulphur content ( $S_{\text{res}}$ ) in hydrodesulphurization products to decrease monotonically depending on the duration of mechanical treatment (Fig. 7). Under the conditions studied, the optimum time of mechanical treatment is equal to 8 h: the value of  $S_{\text{res}}$  reaches a minimum value of 0.005 mass % (see Fig. 7). Therewith, the DBT hydrodesulphurisation rate constant monotonically increases depending on the duration of the MA of starting reagents to attain reaches a maximum value  $k = 0.93 \text{ h}^{-1}$  in the series under investigation (Fig. 8).

The comparative analysis of the efficiency of the catalytic action of these systems with respect to DBT demonstrates that catalyst I (2 h of MA, the ratio between the components 1 : 1 : 5) with a relatively low rate constant ( $k = 0.46 \text{ h}^{-1}$ ) is better than catalyst II, because the former provides a relatively low content of residual sulphur (0.003 mass %). These data are slightly inferior than the parameters of the activity obtained for a reference supported catalyst:  $k = 0.68 \text{ h}^{-1}$ ,  $S_{\text{res}} = 0.002 \text{ mass } \%$ .

At the same time, a high rate constant for the catalyst II is not completely consistent with

the hydrodesulphurisation level observed for the model compound ( $S = 0.005 \text{ mass } \%$ ). This could be caused by increasing the contribution of the processes those occur simultaneously with hydrogenation of the dibenzothiophene ring to promote decreasing the concentration of the DBT in the reaction mixture ( $\lambda = 324 \text{ nm}$ ), but in this case the sulphur remains in the ring. Such processes could be presented, for example, by the reactions of forming the products **A** or **B** those do not belong to the dibenzothiophene series (see Fig. 4).

## CONCLUSION

Therefore, the principal possibility of the single-stage synthesis of massive sulphides catalysts of hydrodesulphurisation of DBT with high hydrodesulphurising ability by the mechanical activation of coarse molybdenum disulfide, cobalt in the presence of nanodiamond has been demonstrated.

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