Investigation of Massive Catalyst based on Molybdenum Disulphide by Simultaneous Thermal Analysis and Mass Spectrometry Methods

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Abstract. The paper presents the results of experimental studies of massive sulfide catalysts by simultaneous thermal analysis and mass spectrometry. It is found that the STA/MS methods are quite informative for testing the catalyst systems based on MoS2 and are useful in identification of the reference features that could be used to predict their activity. It is also shown that the defect structure of molybdenum disulfide formed during mechanical activation is reflected on the DSC curves.

1. Introduction

The development of methods for the synthesis of domestic massive sulphide catalysts for hydrotreating of petroleum fractions is a strategic priority in the field of oil refining to produce high quality distillate fuels. Conventional western technologies allow producing bulk catalysts with a high activity and selectivity for all types of hydroprocessing procedures (hydrogenation, hydrodesulfurization, hydrodenitrogenation, hydrodemetallization, hydrodearomatization, hydroisomerization, hydrodewaxing, hydrocracking) [1]. These multi-stage and energy-intensive methods require the use of large amounts of aqueous solutions of salts-precursors as the active components, which is inevitably accompanied by the formation of substantial amounts of wastewater with toxic anions [2-4]. The use of mechanical activation method to prepare the hydrotreating catalyst systems has a number of advantages, as it allows reducing the number of stages and preparation time, and eliminating the use of aqueous solutions of reagents and organic solvents.

We propose a new promising approach to manufacturing 4-, 3-, 2-, and 1- component massive sulfide catalysts, which is implemented in a single-stage mixing of initial solid-phase reagents under mechanical activation (MA). In this case, MoS_2 is a dimensional inorganic precursor of the active component only and it has to be subjected to dispersion [5]. We have previously shown [6, 7] that the catalysts of this series are capable of providing an ultra-low level of sulfur (about 10 ppm) in a model reaction of hydrogenolysis of dibenzothiophene (DBT) and in the course of hydrorefining the straight-run diesel fraction ($S_{initial} = 2.08\%$).

For 1-component catalysts based on MoS_2, a unique experimental fact was discovered – their activity in the model reaction of dibenzothiophene hydrodesulfurization can be significantly increased

in case of using the trace amounts of polar liquids (S_{res} = 1-3 ppm) during MoS_2 MA-dispersion. There is no answer to the question of the reason for such a high catalytic activity and diagnostics of such systems so far.

It is well known that thermal analysis methods are based on detection of thermal effects which reflect the physical and chemical transformations occurring in the analyzed sample. For example, a simultaneous thermal analysis (STA) allows us to monitor the change in mass, oxidation, decomposition of the sample substance, temperature and enthalpy of the phase transition, the thermal effects of chemical reactions, and to study the kinetics of the reactions [8-10]. A combination of the simultaneous thermal analysis and mass spectrometry (MS-STA) allows us to obtain a lot of additional data on the composition of volatile products.

The aim of this study was to investigate massive sulfide catalysts based on MoS_2 via a simultaneous thermal analysis and mass spectrometry.

2. Experimental

A number of sulfide catalysts were prepared by the solid phase method. The commercial coarse-grained powder of molybdenum disulfide (the content of molybdenum disulfide is 99.72%) was used as a precursor of the active catalyst component. The powder was subjected to mechanical activation in a vertical vibratory mill in the presence of trace amounts of polar liquids (in this case, methanol) and in their absence.

The activity of the catalyst system was evaluated by the residual content of sulfur in the course of hydrogenolysis of a model dibenzothiophene compound which represents the most stable sulfur structures presented in the diesel fraction. The model reaction experiments were performed in an 'AUTOCLAVE ENGINEERS' autoclave with the reactor volume of 100 ml, at a pressure of 3.4 MPa, and a temperature of 340 °C ($S_{initial}$ = 500 ppm).

The samples were analyzed by the STA-MS method using a STA-449C ("Netzsch") apparatus combined with a quadrupole QMS 403C mass spectrometer. Heating was carried out in air (flow rate of 20 ml/min) to 650 ℃ at a heating rate of 10 °C/min. The results of thermogravimetry (TG) and differential scanning calorimetry (DSC) were processed using the 'Proteus Analysis' program.

3. Discussion of Results

It was found out experimentally that in the presence of mono-component catalysts prepared by the solid phase method (Table 1), a complete hydrodesulfurization of dibenzothiophene was observed which had not been reported in the literature. For example, the coarse-grained molybdenum disulfide (catalyst system AK-0) used as a commercial reagent (DMI-7) exhibits certain catalytic activity resulting in a 20% conversion of DBT and a 100 ppm decrease in the residual sulfur content in the reaction mixture (from the initial 500 ppm). The sulfur content in hydrodesulphurizate was reduced by a factor of 5 (down to 100 µl) in the presence of mechanically activated MoS_2. In the presence of trace amounts (100 µl) of a polar liquid (methanol) the MoS_2 monocatalyst exhibits its maximum activity in the model reaction of DBT hydrogenolysis (residual sulfur content 1-2 ppm; AK-60).

Table 1. Composition of catalysts, conditions of their MA and their activity in a model reaction.

Number of sample	Catalyst composition	Time of MA (h)	Residual sulfur (ppm)
AK-0	Commercial MoS_2	-	400
AK-27	Commercial MoS_2	8	105
AK-60	MoS_2+100 µl CH_3OH	8	1-2
AK-71	MoS_2+ 200 µl CH_3OH	8	50
AK-74	MoS_2 + 200 µl CH_3OH	12	6

A slightly higher volume of CH_3OH added to MoS_2 (up to 200 μl) requires longer (by about 4 hours) MA time (Table 1), which is necessary to provide ultra-low sulfur content in the reaction products.

On the other hand, we have to answer the questions on the reason for the threshold effects in the activity of MoS_2 in the presence of trace amounts of CH_3OH and the origin of active centers in the above catalysts. The method of simultaneous thermal analysis and mass spectrometry allowed us to obtain the following additional information on the AC-27, AC-60 and AC-74 catalysts *before* and *after* their participation in a model reaction.

Figures 1 and 3 show typical TG, DTG, and DSC curves using the AC-74 catalyst system as an example. First of all, it should be noted that the mass loss occurs in the temperature region up to 170-280 °C. The calculated content of methanol in the sample is 0.026% which could be hardly measured without special techniques. According to MS spectra, the ions with the following masses: m/e = $18(H_2O^+)$, $12(C^+)$, $2(H_2^+)$, $34(H_2S^+)$, etc. have been identified in gas atmosphere in this temperature region, and an interpretation of their presence in the spectra is difficult. The mass loss of the AC-74 catalyst sample *before* the reaction at the temperature up to 300 °C is 11.19% while *after* the reaction it is 8.66%. The mass changes in MoS_2 within the temperature range above 300 °C are due to its oxidation.

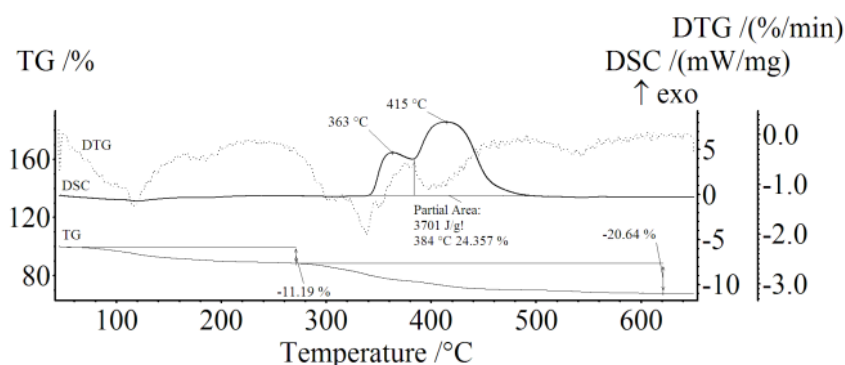**Figure 1.** Results of thermal analysis for AC-74 catalyst *before* to its use in the model reaction; $m_{initial} = 5.61$ mg.
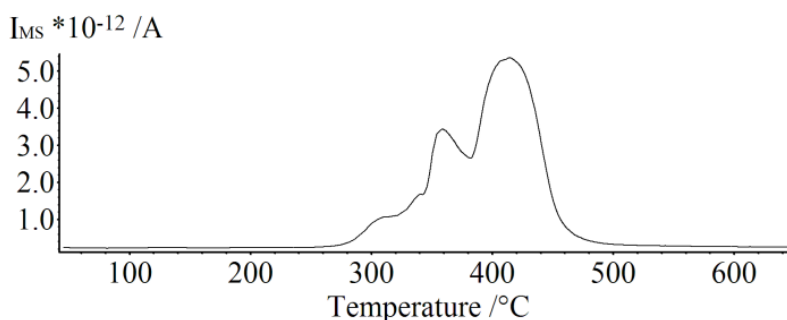

Figure 2. MS spectra with *m/e* = 64 (SO_2^+) for the gas atmosphere during the heating of AC-74 catalyst *before* to the reaction.
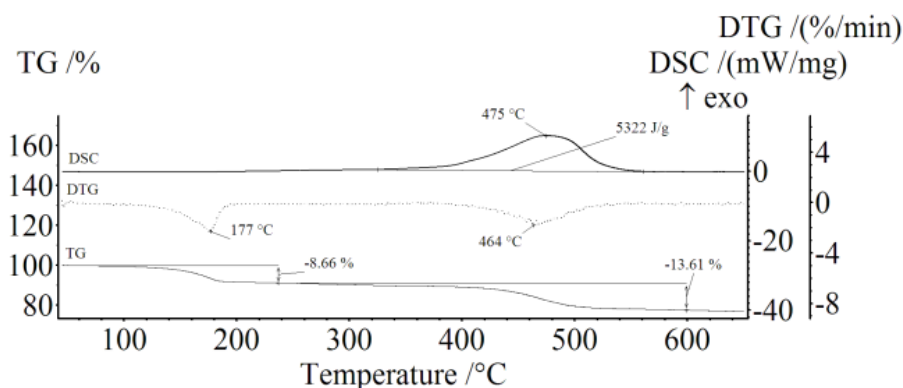
Figure 3. Results of thermal analysis for AC-74 catalyst *after* its use in the model reaction; $m_{initial} = 4.54$ mg.
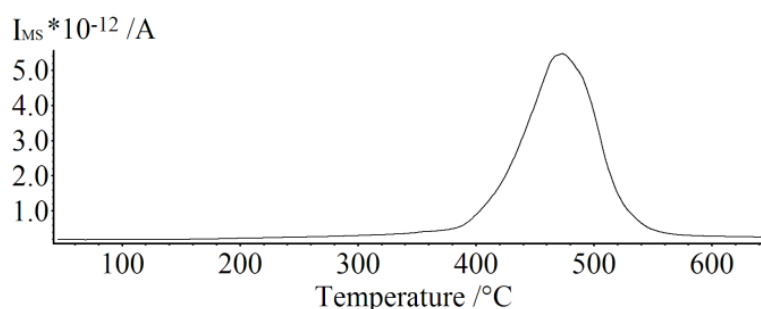

Figure 4. MS spectra with *m/e* = 64 (SO_2^+) for the gas atmosphere during the heating of AC-74 catalyst *after* to the reaction.

According to thermal analysis for all investigated samples, the identical changes of the shape in DSC curves are observed for the catalysts *before* and *after* their use in the model reaction. For example (see Fig. 1, 3), the DSC curve for AC-74 catalyst *before* the reaction is a double-humped curve of heat emission with the temperature maxima of its major peaks at 415 °C and 363 °C (Table 2), while for the AC-60 and AC-27 catalysts, the DSC curves are polymodal. The first low temperature peak in the thermograms for these catalysts disappears *after* the reaction.

Table 2. Temperature peaks on the DSC curves for monocomponent sulfide catalysts.

Catalyst	The temperature of the first peak on the DSC curve *before* the reaction (°C)
AC–27	354
AC–60	377
AC–74	363

One more specific feature of the formal external analysis of the curves should be noted: the peaks of heat emission in the temperature range 300-550 °C (Fig. 1, 3) in the DSC curves repeat the shape of

the mass spectral peaks in the MS curves (Fig. 2, 4). Moreover, these changes are accompanied by mass loss (DTG and TG curves in Fig. 1 and 3). The ratio m/e = 64 is identified as the molecular SO_2^+ ion formed by oxidation of MoS_2. According to the literature data, oxidation of a coarse-grained MoS_2 begins at about 400 °C. For nanodisperse states, the initial oxidation temperature of the substrate can be much lower.

It is well known from the literature [11, 12] that the mechanical activation of the reaction mixture is accompanied by an increase in the number of point contacts, generation of defects, their constant regeneration, multiplication, and migration throughout the entire volume of the reaction mixture. Hence, the broadening of the MS peaks corresponds to a multiple set of different discrete states produced during mechanical activation of MoS_2, which are due to varying degree of bonding of sulfur atoms with Mo and imperfection of its nanocrystallites. The shift of the MS peak temperature from 415 to 475 ºC in Fig. 4 might testify in favour of the initial activity of low-temperature catalytically active centers of MoS_2 and their functioning during the model reaction. In addition to that, there is a reasonable question about the effective lifetime of mono-component catalysts based on molybdenum disulphide in the reactions of DBT hydrodesulfurization in the absence of such centers.

4. Conclusion

Thus, for the first time we have shown a possibility of identifying structure defects formed during mechanical activation using the DSC curves. The experimental results obtained show that the STA/MS method is quite informative for testing the catalyst systems based on MoS_2 and is useful in identification of the reference features that could be used to predict their activity.

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