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High-active hydrotreating catalysts for heavy petroleum feeds: Intentional synthesis of CoMo sulfide particles with optimal localization on the support surface

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ABSTRACT

The method for preparation of high-active catalysts for hydrotreating of vacuum gas oil is described. The method is based on selective incorporation of bimetal Co–Mo complexes into pores of Al_2O_3 exposed to all molecules of the feedstock. The composition, structure and morphology of the resulting surface bimetal sulfide particles are very close to the particles characteristic of the best modern hydrotreating catalysts. The obtained catalyst is very active to hydrotreating of vacuum gas oil and superior to the best of Russian industrial catalysts.

1. Introduction

In the recent years, deepening of oil processing has resulted in an increase in the proportion of distillates of secondary destruction processes (light cycle oil, visbreaking and coker gasoline) in motor fuels. The secondary distillates comprise sulfur, nitrogen and condensed aromatic compounds in much larger quantities than the straight-run distillates. For example, ca. 90% of sulfur in commercial gasoline is supplied with gasoline obtained by catalytic cracking [1]. Even though various methods are developed for desulfurization of oil distillates [1,2], the most practiced industrial process is the catalytic hydrotreating. There are two ways for minimizing the sulfur content in the catalytic cracking gasoline; these are either gasoline hydrotreating or hydrotreating of vacuum gas oil as the main feedstock for catalytic cracking. The latter is more promising because the gasoline hydrotreating causes inevitably a decrease in the octane number [1–3], while the fine hydrotreating of vacuum gas oil, apart from synthesis of low-sulfur gasoline, has a favorable effect on the operation of catalytic cracking units [3,4]. Thus, sulfur removal from heavy oil is an important process for meeting sulfur regulations in transportation fuels. In the recent studies the questions of heavy oil feed and products properties characterization by advanced analytical methods and understanding about heavy oil desulfurization and denitrogenation reactions chemistry are intensively developed [5,6], the new methods for the heavy oil hydrotreating catalysts preparation are continuously improved as well. The strong inhibition effect from three and larger ring aromatic compounds on the different hydrotreating reactions of heavy oils was revealed [5,6]. Thereby, the new catalysts for VGO hydrotreating should provide high activity in the hydrogenation, denitrogenation and desulfurization reactions.

At present it is commonly accepted that the active phase of hydrotreating catalysts comprises MoS_2 nanoparticles with cobalt or nickel atoms localized in their edge faces [7–10], some particular points on the structure of the active sites are so far disputable. The necessary textural parameters of the supports to be used for hydrotreating of hydrocarbon feedstock of a given fractional composition also are well known [11]. Therefore, the recent R&D works on optimization of the hydrotreating catalysts have been focused on two main problems:

1. Optimization of methods for preparation and activation to produce catalysts containing only hydrotreating active sites as surface compounds.
2. Intentional development of supports with the necessary texture for hydrotreating of particular oil fractions to provide exposing the surface active sites to S- and N-compounds with certain molecular size.

Evidently, the effective hydrotreating of middle and heavy oil feeds is only possible over catalysts bearing the active sites at the maximal surface concentrations, the necessary condition being that the active sites reside in the support pores which are exposed to the largest sulfur-containing and aromatic molecules of the oil feed [12,13].

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In the present work, a new comprehensive approach is suggested to provide synthesis of high-active catalysts for deep hydrotreating of vacuum gas oil. It is based on the following components:

1. The use of a support with the specific surface area more than 200 m^2/g and predominant pore diameter ca. 120 Å. This is the preferable support for hydrotreating of middle oil distillates and vacuum gas oil [11].
2. The catalyst preparation is based on the application of bimetal Co–Mo compounds with the same metal stoichiometry as the active hydrotreating sites. These compounds should not change their structure upon supporting on Al_2O_3, their molecular size should allow all the active component to be arranged in the catalyst pores exposed to all aromatics, S- and N-containing compounds of the feed used.
3. Application of those methods for the catalyst activation, which provide the selective transformation of the supported bimetal compounds into the species active for the hydrotreating reactions.

2. Experimental

2.1. Catalyst preparation

The support was Al_2O_3 developed deliberately by JSC Promyshlennye Katalizatory (Ryazan, Russia) to prepare catalysts for hydrotreating of middle oil distillates and vacuum gas oil. The support was trilobe shaped (Ø = 1.5 mm, l = 3–6 mm) and characterized by the specific surface area of 240 m^2/g, pore volume of 0.74 cm^3/g, average pore diameter of 122 Å. The support was modified by impregnating it with an aqueous H_3BO_3 solution followed by drying at 200 °C.

Catalysts were prepared by impregnating the support with an aqueous solution of a bimetal CoMo compound. The CoMo compound was synthesized from the ammonium salt of the tetrameric citrate anion $[Mo_4(C_6H_5O_7)_2O_{11}]^{4-}$, which was prepared via dissolution of 44.8 g (0.234 mol) of citric acid and 57.92 g (0.328 mol of Mo) of ammonium heptamolybdate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) in a small amount of distilled water, followed by the addition of more water to obtain exactly 200 ml of solution. The solubilization of solid $Co(CH_3COO)_2\cdot 4H_2O$ $4H_2O$ in $(NH_4)_4[Mo_4(C_6H_5O_7)_2O_{11}]$ containing solution in proportions equivalent to a Mo/Co = 2 atomic ratio results to the formation of bimetal compound with Co^{2+} cations coordinated towards molybdenum-containing tetranuclear anion $[Mo_4(C_6H_5O_7)_2O_{11}]^{4-}$, call it Co_2Mo_4citr. The results of its characterization by NMR, EXAFS, FTIR, Raman spectroscopy are given elsewhere [14,15]. Fig. 1 shows its supposed structure without the solvation sphere and cobalt-coordinated water molecules.

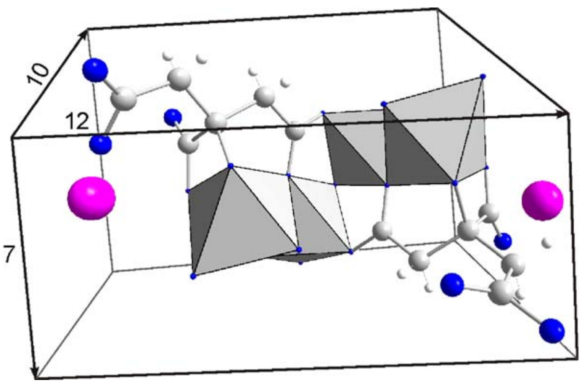

Fig. 1. Tentative structure of the bimetallic Co–Mo complex framed with parallelepiped (general parameters 7 Å × 10 Å × 12 Å).

The supported catalyst was obtained via the impregnation of alumina in vacuum with Co_2Mo_4citr solution. The impregnation procedure was carried out with intermittent stirring of alumina granules in a solution volume that was 25% greater than the water sorption capacity of the 'dipped-in-support' granules. After 20 minutes of stirring, the supernatant was drained out and the solid fraction was dried at 110 °C for 4 h. Hereinafter, the catalyst is referred to as Co_2Mo_4citr/Al_2O_3.

To determine the textural parameters and metal contents, the catalyst was calcined in air at 550 °C for 2 h. Thus treated catalyst comprised 10.30% Mo, 3.16% Co and 0.70% B, it is referred to as $CoMoO/Al_2O_3$. To determine textural parameters only, the catalyst Co_2Mo_4citr/Al_2O_3 was sulfided in H_2S at the volume hourly space velocity of 500 h^{-1} at 400 °C for 2 hours. Such a catalyst is referred to as $CoMo(H_2S)/Al_2O_3$.

The catalyst dried at 110 °C was used for the other studies.

2.2. Catalyst characterization

Textural properties of catalyst and support were determined by nitrogen physisorption using an ASAP 2400 (USA) instrument.

EXAFS spectra of the Mo–K edge were obtained at the EXAFS Station of the Siberian Synchrotron Radiation Center (Novosibirsk) under the conventional transmission mode [16]. The storage ring VEPP-3 with the electron beam energy of 2 GeV and the average stored current of 100 mA was used as the source of radiation. The spectrometer has the Si(1 1 1) cut-off crystal-monochromator and two proportional ionization chambers as detectors. For each sample the oscillating portion of EXAFS spectra ($\chi(k)$) was treated in the form of $k^2\chi(k)$ at the wave number interval of 2.5–14.0 $Å^{-1}$. The EXAFS spectra simulations for retrieving the structure data were performed using the standard procedure by VIPER code [17]. The FEFF7 program was employed to fit the parameters of scattering [18].

High-resolution transmission electron microscopic (HRTEM) images were obtained on a JEM-2010 electron microscope (JEOL, Japan) with a lattice-fringe resolution of 0.14 nm at an accelerating voltage of 200 kV. The high-resolution images of periodic structures were analyzed by the Fourier method. Local energy-dispersive X-ray analysis (EDXA) was carried out on an EDAX spectrometer (EDAX Co.) fitted with a Si (Li) detector with a resolution of 130 eV. Samples to be examined by HRTEM were prepared on a perforated carbon film mounted on a copper grid. The size of MoS_2 particles and the average number of layers in the package were determined using four different fragments of the sample under study, a total number of characterized particles being equal to 500.

The Raman spectra were recorded at room temperature in the range of 3600–100 cm^{-1} using FT-Raman spectrometer RFS 100/S BRUKER (Germany). The used excitation source was the 1064 nm line of Nd-YAG laser operating at power level of 100 mW.

X-ray photoelectron spectra (XPS) were recorded using a spectrometer SPECS (Germany) with a PHOIBOS-150 hemispherical energy analyzer and AlK_α irradiation ($h\nu$ = 1486.6 eV, 200 W). Binding energy scale was preliminarily calibrated by the position of the peaks of $Au4f_{7/2}$ (84.0 eV) and $Cu2p_{3/2}$ (932.67 eV) core levels. For spectra recording the samples were supported to the conductive scotch tape. The internal reference method was used for correct calibration of photoelectron peaks. For this C1s peak (E_b = 284.8 eV) corresponding to the surface hydrocarbon-like deposits (C–C and C–H bonds) accumulated on the surface during the storage in the atmosphere. A low energy electron gun (FG-15/40, SPECS) was used for the sample charge neutralization.

In addition to the survey photoelectron spectra, more narrow spectral regions Al2p, Al2s, S2p, S2s + Mo3d, C1s, O1s and Co2p were recorded. For the survey spectra the pass energy of the analyzer was 50 eV, while 10 eV for the narrow spectral regions.

Analysis of the individual spectral regions allowed determining the values of binding energies of the peaks, identifying the chemical state of the elements, as well as calculating the ratios of the atomic concentrations of the elements on the catalyst surface. The Shirley method was used for the background subtraction in the photoelectron spectra.

2.3. Testing of the hydrotreating catalyst

A three-phase down-flow reactor (internal diameter 16 mm, isothermal zone 300 mm in length) was used for the catalyst sulfidation and characterization of their catalytic activity for hydrotreating of vacuum gas oil (VGO). The feed was supplied to the reactor using a HPLC pump; hydrogen was portioned using an automated Bronkhorst flow meter. In each test 10 ml of catalyst granules (Ø = 1.5 mm, *l* = 3–6 mm) were mixed with fine carborundum particles (fraction 0.25–0.5 mm) at the ratio 1:1 and loaded in the isothermal zone of the reactor [19]. Carborundum is also loaded below and above the catalyst bed.

The catalyst was presulfided in a reactor using a mixture of straight-run gas oil (0.8% S, FBP-340 °C) and dimethyldisulfide. The total of sulfur content in the sulfiding mixture was 1.4%. The process was achieved in the temperature range of 230–340 °C at 3.5 MPa, the liquid hourly space velocity (LHSV) of the sulfiding feed was 2 h^{-1} and hydrogen/oil ratio equaled 300. That was the procedure developed intentionally for sulfidation of the catalysts contained bimetal Co_2Mo_4citr [20,21]. The sulfide catalysts are referred to as $CoMoS/Al_2O_3$.

VGO hydrotreating was achieved at 360–400 °C, 5.0 MPa, LHSV being 1 h^{-1} and hydrogen/feed ratio equaled to 400.

Initial VGO properties were as follows: boiling range 360–500 °C, density 0.92 g/cm^3 at 20 °C, sulfur content 2.12%, nitrogen content 1476 ppm, hydrogen content 12.14%, atomic ratio H/C = 1.69.

The sulfur content in the liquid products was measured by a X-Ray Fluorescence Analyzer LabX3500SL (from Oxford Instrument).

The total of nitrogen content in vacuum gas oil and its hydrotreating products was determined using an analyzer Antek 9000NS.

The weight fraction of hydrogen in vacuum gas oil and its hydrotreating products was determined using a low resolution pulse NMR spectrometer MQC-23 (from Oxford Instrument).

The density of the initial vacuum gas oil and its hydrotreating products was determined using a digital densimeter Mettler Toledo Densito 30PX.

3. Results and discussion

3.1. Modification of the carrier with boron

In this paper we used aluminum oxide modified with boron, the boron content in the catalyst was 0.7%, which corresponds to molar ratio B/Al = 0.04. Although the purpose of this work was not to study the influence of boron on the properties of the catalyst, it should be noted that the concentration of boron and the method of its introduction to the catalyst are not random, and it was selected on the basis of our preliminary experiments and analysis of literature data. Previously, we have modified with boron alumina with specific surface area 240 m^2/g by impregnating of aqueous solution of H_3BO_3 followed by drying at 200 °C. The prepared samples contained up to 2% boron. After subsequent deposition of bimetallic Co–Mo compound and samples sulfidation in accordance with the techniques described in this paper we found that the catalysts containing 0.6–0.8% boron are more active in hydrodesulfurization of diesel fuel compared with samples contained higher or lower concentration of boron. Obtained results are in good agreement with literature data [22–30]. In the cited papers, regardless of the method of catalyst preparation, maximal hydrodesulfurization activity corresponds to the concentration of boron in the catalyst 0.6–1.0% [22–29] or molar ratio of B/Al = 0.04 [30].

Boric acid at these concentrations reacts predominantly with the base Al–OH groups with the formation of Al–OB bonds [24,26] and it is contained in the catalyst in the form of BO_4 surface species [30]. The positive effect of boron on the hydrodesulfurization catalyst activity is to increase the surface acidity, as a result the interaction of Co and Mo with the carrier is decreased [24–26,28–30]. Thereby, the undesirable bulk MoO_3 or $CoMoO_4$ species are not formed during the oxide precursors preparation [30] and the quantity of cobalt localized at the edge planes of MoS_2 particles is increased in the sulfide form of catalyst [23]. Simultaneously Co_9S_8 formation is also decreased [26], as well as a more complete sulfidation of the supported metals is revealed in comparison with non-boron-containing catalysts [26,27]. Below, in Section 3.3 we have demonstrated that supported Co and Mo in the resulted catalysts are completely sulfided and undesirable Co_9S_8 particles are not segregated.

The increase of boron concentrations in the catalyst above 1% leads to a decrease of catalytic activity due to the active component sintering [22,24,26,27]. It should be noted that according to the data [22,24,26] the introduction of 0.6–1.0% of boron into the catalyst does not lead to the noticeable changes in surface area and pore volume, compared with non-boron-containing catalyst. Clearly, boron at these concentrations is dispersed on the alumina without noticeable changes of the textural characteristics.

3.2. Localization of the active component in the catalyst pores

The atomic Co/Mo ratio is equal to 0.5 both in the initial bimetal compound and in typical high-active catalysts for hydrotreating, see, e.g., Refs. [7–9,31]. Co_2Mo_4citr (Fig. 1) is a large enough molecule with the geometrical size (without its solvate sphere) inscribed in a parallelepiped 7 Å × 10 Å × 12 Å. This size is comparable to the size of substituted phenanthrothiophenes and benzonaphthothiophenes, which are some of more difficult to transform and biggest sulfur-containing components of vacuum gas oil [1,13,32]. While Co_2Mo_4citr preserves its structure when supported on Al_2O_3 [14,15,33], the bimetal complex cannot penetrate into narrow pores and, as a result, is only localized in large pores of the support. An evidence of this conclusion is that the initial support and catalysts $CoMoO/Al_2O_3$ and $CoMo(H_2S)/Al_2O_3$ have different textural parameters (Table 1; Fig. 2).

The specific surface area and pore volume, as well as diameter of pores, are lower in the catalyst $CoMoO/Al_2O_3$ than in the initial support. There may be two reasons for the difference: either deposition of cobalt and molybdenum compounds on the catalyst surface or partial sintering of the support during calcination the $CoMoO/Al_2O_3$ catalyst at the temperature close to the temperature of phase transitions of alumina [34].

Table 1
Textural properties of the carrier, oxide and sulfide $CoMoO/Al_2O_3$ catalysts.

Sample	Surface area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (Å)
Al_2O_3	240	0.74	122
$CoMoO/Al_2O_3$	191	0.54	113
$CoMo(H_2S)/Al_2O_3$	190	0.53	111

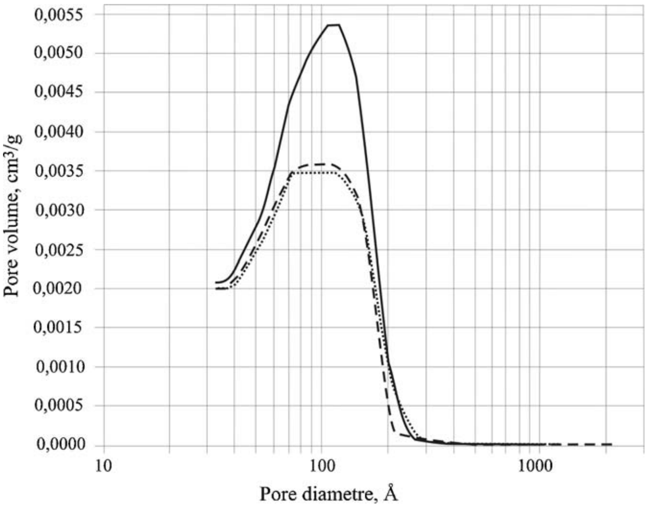

Fig. 2. Pore size distribution. Solid line: Al_2O_3, dashed line: $CoMoO/Al_2O_3$, dotted line: $CoMo(H_2S)/Al_2O_3$.

If the calcination has not caused sintering of the catalyst support to decrease its pore size, a total decrease in the catalyst pore volume in respect of that in the support must correlate with the volume of Co and Mo compounds introduced. We assume, for simplifying calculations, that metals are in the form of MoO_3 and CoO in the $CoMoO/Al_2O_3$ catalyst, and their porosity is negligible in comparison to that of the support. The chemical composition of the catalyst calcined at 550 °C (expressed as oxide percentage) is: 15.45% MoO_3; 4.02% CoO; 2.25% B_2O_3 and 78.28% Al_2O_3. The pore volume is 0.74 cm^3/g in the initial alumina. If the pores were absolutely free in Al_2O_3, the pore volume of the support comprised in 1 g of the catalyst would equal 0.579 cm^3. The experimentally measured pore volume in the catalyst is 0.54 cm^3/g (Table 1). Hence, there is a 0.039 cm^3 decrease in the pore volume of the catalyst in comparison to that of the support.

From reference data on density (4.69 g/cm^3 MoO_3, 5.7–6.7 g/cm^3 CoO, average 6.2 g/cm^3), 1 g of the catalyst comprises 0.0329 cm^3 MoO_3 and 0.0065 cm^3 CoO, in total 0.0394 cm^3. Chemical analysis gives the volume 0.0394 cm^3 of Co and Mo oxides introduced to the catalyst; this agrees well with a decrease in the pore volume of Al_2O_3 in the catalyst determined from the textural parameters (0.039 cm^3). Hence, the decrease in the pore volume of the $CoMoO/Al_2O_3$ catalyst *vs.* support is accounted for by the deposition of Co and Mo compounds in the pores but not by the sintering during its calcination.

Supporting of Co_2Mo_4citr on Al_2O_3 results in a considerable decrease in the volume of pores with diameter 60–160 Å but in a negligible decrease of the other pores in volume (Fig. 2). It seems like the bimetal compound resides namely in the 60–160 Å pores. This conclusion also is argued for by the fact that the average pore diameter is decreased by 9 Å in the catalyst $CoMoO/Al_2O_3$ in comparison to that of the support (Table 1): if the narrow pores were filled or their necks blocked, the average pore diameter would increase but this is not the case. On sulfidation, the active component remains localized in the same pores as the bimetal precursor (the textural parameters of samples $CoMoO/Al_2O_3$ and $CoMo(H_2S)/Al_2O_3$ are fully identical).

Thus, the use of Co_2Mo_4citr allows the catalysts to be prepared, which contain oxide and sulfide compounds of Co and Mo as localized predominantly in the pores with 60–160 Å diameter; as a result, all the active component appears exposed to the largest and hard-to-transform 3+ rings aromatics and sulfur-containing molecules in VGO [1,13,32].

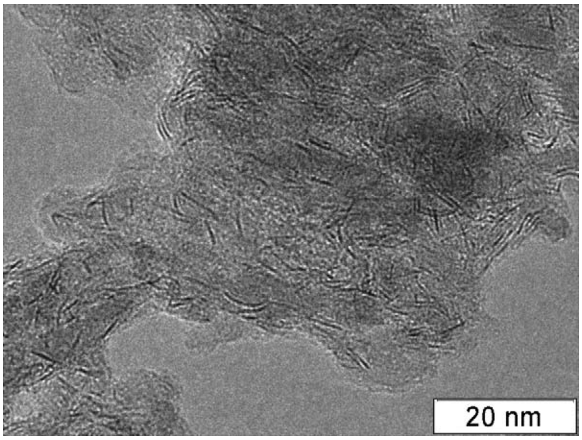

Fig. 3. TEM micrographs of liquid-phase sulfided $CoMoS/Al_2O_3$ catalyst.

3.3. Structure of the active component

Co_2Mo_4citr/Al_2O_3 was sulfided by a mixture of straight-run gas oil and dimethyldisulfide (the mixture composition was typical of sulfiding mixtures for hydrotreating catalysts [35]) under specially chosen conditions [20,21]. The molar ratio S/Mo = 2.0 in the resulting catalyst $CoMoS/Al_2O_3$ indicates the complete conversion of initial oxygen-containing compounds to MoS_2.

A high-resolution transmission electron microscopic (HRTEM) image of a typical surface fragment of the $CoMoS/Al_2O_3$ catalyst is shown in Fig. 3. From the local energy-dispersive X-ray analysis (EDXA) data, Co, Mo and S are evenly distributed through the catalyst surface, the element concentrations, within the experimental accuracy, being corresponding to the atomic ratio Co/Mo/S = 1/2/4. There are visual MoS_2 particles (55 layers per 1000 nm^2 of the catalyst surface) distributed evenly over the alumina surface. The particles are 29 Å in average length at the average number of layers equal to 1.68 in the package. Generally, the results obtained are in good agreement with literature data on the CoMoS phase, which is the main component of high-active hydrotreating catalysts after they have been subjected to liquid-phase sulfidation [8,36]. Note that many of individual MoS_2 particles are distorted in shapes, and non-parallel arrangement of layers is characteristic of some packages. While CoS_x crystallites are not observed in the images, sulfidation does not cause cobalt segregation in the case under consideration but does with some commercial $Co–Mo/Al_2O_3$ hydrotreating catalysts [37].

Fig. 4 shows Raman spectra of the $CoMoS/Al_2O_3$ catalyst and the reference sample of crystalline MoS_2. Intense peaks assigned to vibrations of supported MoS_2 [38] are observed in the region of 450–150 cm^{-1} in the spectrum of the catalyst. In comparison to the spectrum of bulk MoS_2, combinational scattering lines are strongly broadened and shifted to the low-frequency region in the spectrum of the catalyst. Probably, the reason is the presence of distorted monolayer MoS_2 particles and packages with non-parallel layer orientation which are detected in HRTEM images of the catalyst. Surface MoS_2 particles are much more disordered than crystalline molybdenum disulfide, and this is exactly what we see in the spectra.

Again, the Raman spectra of the sulfide samples under study do not show any line at 1000–800 cm^{-1}, which could be assigned to any surface compounds containing molybdenum in oxygen surrounding, for example the ones described in Ref. [39]. This indicates unambiguously that the supported metals are only composed of sulfide compounds.

XPS data also support the conclusion about the complete sulfidation of the metals in $CoMoS/Al_2O_3$ and the formation of surface bimetal sulfides or the CoMoS phase.

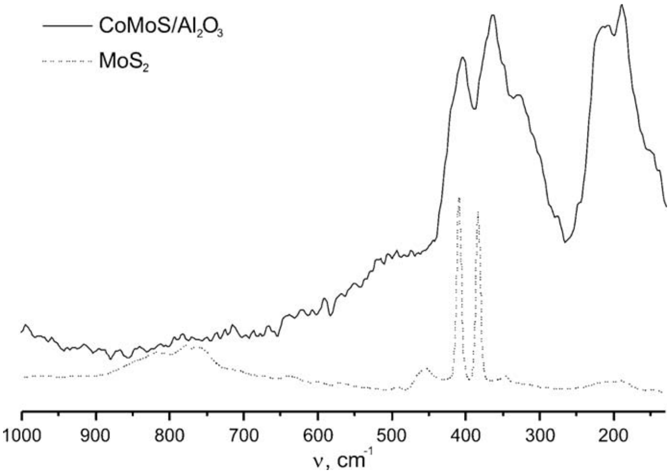

Fig. 4. Raman spectra of CoMoS/Al_2O_3 and bulk MoS_2 in the range of 1000–130 cm^{-1}.

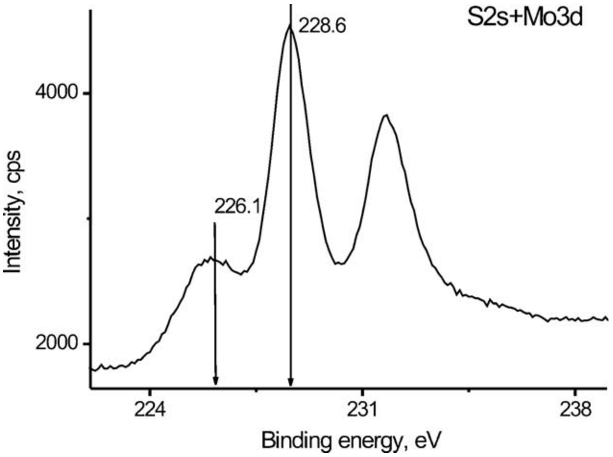

Fig. 5. S2s and Mo3d XPS photoelectron spectra of the CoMoS/Al_2O_3 catalyst.

Fig. 5 shows an XPS spectrum of CoMoS/Al_2O_3, levels S2s + Mo3d. A peak at binding energy BE = 226.1 eV is assigned to sulfur (S2s). A peak of molybdenum at BE = 228.6 eV is characteristic of sulfide molybdenum in MoS_2, the molybdenum state is formally Mo^{4+}. Inspection of the presented spectra allows the presence of molybdenum in an oxide surrounding to be absolutely excluded. In S2p spectra, a peak at BE = 162.0 ± 0.2 eV is characteristic of sulfides containing sulfur as S^{2-}.

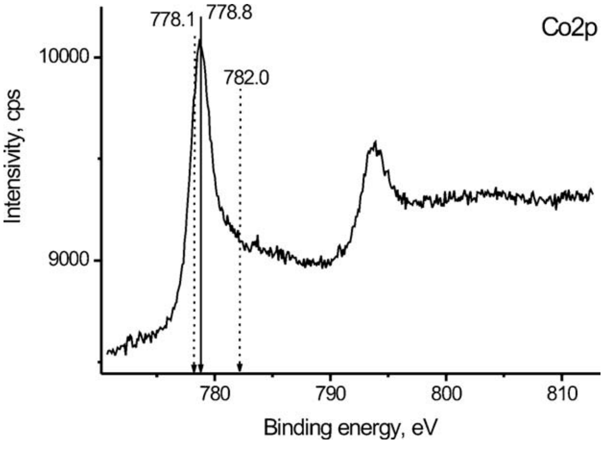

Fig. 6. Co2p XPS photoelectron spectra of the CoMoS/Al_2O_3 catalyst.

Fig. 6 shows the Co2p spectrum. The binding energy Co2p equals 778.9 ± 0.1 eV that is characteristic of cobalt in bimetal CoMo sulfide particles [36,40]. The absence of peaks at BE = 781–782 eV and BE = 778.1 eV indicates the absence of cobalt oxides and sulfides, Co_9S_8 [26,39,41,42]. In accordance with data given elsewhere [40], the differences BE($Co2p_{3/2}$)–BE(S2p) and BE($Co2p_{3/2}$)–BE($Mo3d_{5/2}$) can be used as the criterion to determine if there are bimetal sulfides or Co_9S_8. With the samples under study, differences ΔBE equal to 617 and 550.2 eV, respectively, are in good agreement with the data on bimetal sulfides where cobalt atoms are arranged at edge planes of MoS_2 packages [36,40,42].

The above XPS data lead to conclude about complete sulfidation of the surface bimetal compounds and the formation of particles of bimetal CoMo sulfide phase on the catalyst surface [41].

The above described results agree well with the relevant EXAFS data (Figs. 7 and 8).

There are two main peaks in the Mo–K edge EXAFS spectrum of CoMoS/Al_2O_3. One of the peaks relates to the distance Mo–S = 2.40 Å (coordination number 5.6), and another to the distance Mo–Mo = 2.61 Å (coordination number 3.1) that is in good agreement with the data on bulk MoS_2. Fig. 8 presents the experimental Co–K edge curve of CoMoS/Al_2O_3 and the curve obtained by modeling. Processing of the experimental data allows peaks related to distances Co–S = 2.22 Å (c.n. 4.0) and

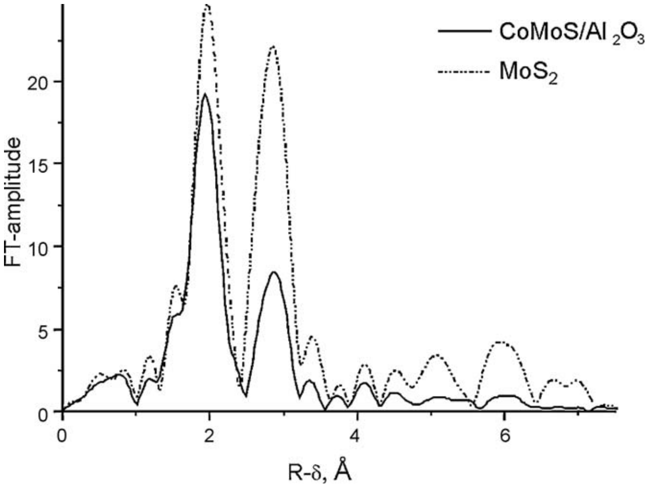

Fig. 7. Fourier transform of Mo–K edge EXAFS spectra for CoMoS/Al_2O_3 (bulk) MoS_2.

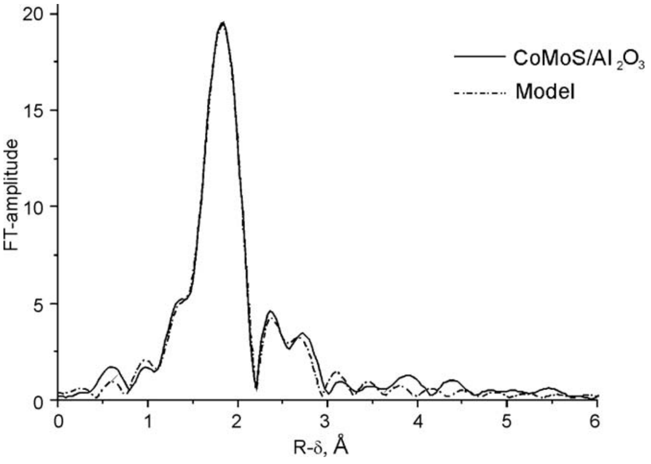

Fig. 8. Fourier transform of Co–K edge EXAFS spectra for CoMoS/Al_2O_3.

Table 2
The results of VGO hydrotreating activity of the CoMoS/Al_2O_3 catalyst.

T, °C	Content of S, ppm	Degree of desulfurization, %	Content of N, ppm	Degree denitration, %	Density, g/cm^3	Content of H, %	Atomic ratio H/C
Initial VGO	21181	–	1476	–	0.9200	12.14	1.69
360	407	98.08	655	55.6	0.8932	12.87	1.76
380	164	99.99	399	72.9	0.8906	12.94	1.77
400	49	>99.99	231	84.3	0.8750	13.01	1.78

P = 5.0 MPa, LHSV = 1 h^{-1}, H_2/feed ratio = 400/1.

Co–Mo = 2.80 Å (c.n. 0.7) to be identified in the curves. The data obtained on the environment about cobalt and molybdenum atoms fit literature data on the distances and coordination numbers of CoMo sulfide catalysts [9,43–45]. The Co–S c.n. = 4 relates to the square-planar coordination of sulfur atoms about Co. Such coordination can only exist when the cobalt atoms reside at the edge plane of molybdenum disulfide. The Co coordination to the basal plane of the MoS_2 package needs smaller coordination numbers [9]. An additional argument for the Co localization in the edge plane of MoS_2 is the presence of two extra peaks at $(R - \delta)$ = 3.7–4.7 Å in the Co–K edge curve, which result from the double scattering similar to that described elsewhere [46].

The set of data obtained with the CoMoS/Al_2O_3 catalysts lead us to conclude that all Co and Mo atoms here are constituents of bimetal sulfides, while characteristic properties of the catalyst surface are as follows:

1. MoS_2 particles are evenly distributed over the support surface. The particles are 29 Å in average length, the average number of layers in the package equals 1.68, and there are ca. 55 layers of MoS_2 per 1000 nm^2 of the catalyst surface.
2. There is a bimetal sulfide compound in the catalyst. The sulfide components are at the atomic ratio Co/Mo/S = 1/2/4, the binding energies of electrons in Co, Mo and S, are typical of bimetal sulfides with cobalt atoms at the edge planes of the MoS_2 package.
3. The catalyst is free of oxygen-containing Mo compounds and free of cobalt oxides and sulfides differing from the CoMoS phase.
4. In the bimetal sulfides, the Mo–S, Mo–Mo, Co–S and Co–Mo distances and coordination numbers are typical of high-active hydrotreating catalysts bearing MoS_2 packages with cobalt atoms at their edge planes.

3.4. Catalytic properties for VGO hydrotreating

The catalyst was tested in the process of VGO hydrotreating under conditions typical of hydrotreating of catalytic cracking feeds [1,4,8] except hydrogen pressure: 5.0 MPa in our experiments *vs.* 6.9–20.7 MPa reported in Refs. [1,4,8]. The results obtained are shown in Table 2. The analysis of the presented results allows us to conclude that the prepared catalyst provides effective removal of condensed aromatics, S- and N-containing compounds of VGO. The results were compared to the data on VGO hydrotreating over most used Russian commercial hydrotreating catalysts RK-442, GP-497, GR-24 M, NKYu-220, NKYu-300 [47–49]. In the cited works, the feed was a lighter VGO with density 0.900-0.915 [47] and 886 g/cm^3 [48], and the process was conducted at a larger hydrogen/feed ratio: 500 m^3/m^3 [49] and even 800 m^3/m^3 [48]. Even though the conditions were more favorable, none of the reported catalyst provided the degrees of desulfurization and denitrogenation, as well as the feed/product density ratios close to those obtained in the presented work (see Table 2). For example, the best of those catalysts, GR-24 M [48], provided the desulfurization degree of 91–94% and denitrogenation degree of 45–54% at the temperature range 340–420 °C, while the difference between the product and feed densities was no more than 1.9%.

Thus, the CoMoS/Al_2O_3 catalyst we propose is much superior in VGO hydrotreating to the most practice Russian commercial hydrotreating catalysts.

4. Conclusions

The present paper describes method for preparation of high-active catalyst for hydrotreating of vacuum gas oil. The said method is the selective introduction of active metals – Co and Mo – into support pores exposed to the largest and hard-to-transform sulfur-containing molecules of the oil feed followed by selective transformation of the supported metals into bimetal sulfides which are active sites of the hydrotreating catalysts.

To prepare the catalyst, a bimetal complex compound synthesized in a solution by coordinating Co^{2+} cations to the $[Mo_4(C_6H_5O_7)_2O_{11}]^{4-}$ anion was used. The support contained 0.7% of boron and had pores of the size optimal for VGO hydrotreating. The bimetal complex was supported by low-temperature impregnation and dried at 110 °C. This procedure provided preservation of the precursor structure on the support surface, as well as allowed the active component to be localized in the pores of the required size.

Sulfidation of the catalyst under specially chosen conditions produced bimetal sulfides with the composition, structure and morphology typical of the currently employed best hydrotreating catalysts.

The resulting VGO hydrotreating catalyst is much superior in activity to the best Russian commercial catalysts tested under similar conditions.

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