



# Investigation of spillover effect in hydrotreating catalysts based on $\text{Co}_2\text{Mo}_{10}$ — heteropolyanion and cobalt sulphide species



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## ABSTRACT

$\text{Co}_2\text{Mo}_{10}/\text{Co}_x/\text{Al}_2\text{O}_3$  catalysts were synthesized from the ammonium salt of  $[\text{Co}_2\text{Mo}_{10}\text{O}_{38}\text{H}_4]^{6-}$  anion supported on alumina modified with various amount of cobalt sulphide. The catalysts were analyzed using X-ray powder diffraction,  $\text{N}_2$  physisorption, high-resolution transmission electron microscopy and X-ray photoelectron spectroscopy. The catalysts were tested in the hydrodesulphurization (HDS) of dibenzothiophene and 4,6-dimethyldibenzothiophene and the hydrodenitrogenation (HDN) of quinoline. The presence of cobalt sulphide particles on the catalysts surface affects catalytic properties significantly, whereas the structure of the active phase remains constant. The catalytic activity, selectivity and turnover frequency during the HDS and HDN reactions depend on the amount of modifier (cobalt sulphide) in the  $\text{Co}_x/\text{Al}_2\text{O}_3$  supports and can be explained by hydrogen spillover effect. The model of HDS reaction over  $\text{Co}_2\text{Mo}_{10}/\text{Co}_x/\text{Al}_2\text{O}_3$  catalyst involving hydrogen spillover was established. The obtained results allow us to focus attention on the role of the cobalt sulphide particles on the surface of hydrotreating catalysts.

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## 1. Introduction

Heteroorganic compounds present in motor fuels are severe environmental contaminants and have bad influence on human health [1]. Gasoline exhaust remains are classified as “possible” carcinogen [2]. In this regard, countries all over the world have introduced stringent requirements on the pollutants (sulphur-, nitrogen-containing and polycyclic aromatic compounds) content in motor fuels. The 15 ppm sulphur specification for ultra low sulphur diesel (ULSD) fuel has been introduced in the USA since 2007 as well as “Sulphur-free” diesel and gasoline fuels with S content  $\leq 10$  ppm have become mandatory in European Union since 2009. According to Brazilian ecological requirements, the amount of sulphur in diesel has been limited to 10 ppm since 2013 [3,4]. Along with that new European regulations [5] will set tighter emission limits, known as Euro 5 and Euro 6, of atmospheric pollutants such as particulates and nitrogen oxide.

The hydrotreating (HDT) of petroleum fractions is the central refining process in order to produce clean fuels that meets the actual ecological requirements. The major way to improve effectiveness of hydrotreating process is the development of new hydrodesulphurization (HDS) catalysts. For this purpose, the

studies devoted to the HDS catalysts development raise considerable interest [6–8]. The major part of industrial HDT catalysts are supported  $\text{Co}(\text{Ni})\text{Mo}(\text{W})/\text{Al}_2\text{O}_3$  systems, which can contain other elements. Today it is a well-known fact that the active phase of HDT catalysts is composed of molybdenum disulphide ( $\text{MoS}_2$ ) promoted with cobalt and/or nickel atoms [9–12]. Various approaches aimed at changing the active phase composition, the promoter/molybdenum ratio, and the support nature were proposed to improve the catalytic properties [12–16].

Recently heteropolycompounds (HPCs) have been widely used as precursors of the active phase of the HDS catalysts. Different types of HPCs with Keggin [17–20] or Anderson [17,20–29] structures were proposed as precursors instead of commonly used ones. The main advantage of HPCs over conventional precursors is the presence of promoter 3d-metal as a heteroatom in heteropolyanion (HPA) that provides the molecular contact between Mo and promoter. The HPCs composition and heteroatom nature determined the final catalytic properties of the HDS catalysts [17,20,25,30]. The use of HPAs with higher Co/Mo ratio than in Anderson type  $\text{XMo}_6\text{HPA}$  leads to enhancement of the promoting effect in CoMo catalysts [17,24,28,30–34]. However, the use of HPAs does not allow to increase the Co/Mo ratio up to optimal 0.5 value [7,8]. Previously it was shown that catalysts prepared with  $\text{Co}_2\text{Mo}_{10}\text{HPA}$  demonstrate better results in the HDS reactions than other counterparts [24,29,30,34,35]. Improved catalytic properties of the catalysts prepared with the  $\text{Co}_2\text{Mo}_{10}\text{HPA}$  are caused by the active phase

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morphology and composition. The use of  $\text{Co}_2\text{Mo}_{10}\text{HPA}$  provides an opportunity to prepare HDS catalysts with highly effective active sites with enhanced TOF values [26]. In spite of high performance of CoMo active sites formed from  $\text{Co}_2\text{Mo}_{10}\text{HPA}$  integral activity of the HDS catalysts might not be enough to produce ULSD at conventional conditions. Hence, a lot of studies are focused on improving catalytic properties of the sulphide CoMo-catalysts.

Numerous researches are aimed at improving the catalytic properties of the catalysts prepared with HPCs. Higher values of the promotion ratio in the catalysts can be reached using various organic additives and chelating agents [26–28,36,37] or by modifying the catalyst support with promoter metals [38–41]. Nonmetal and noble metal modifiers were also investigated in order to improve catalytic properties of the HDT catalysts [42–47]. The synergetic effect was discovered during the investigation of the support surface modification with transition metals [41]. This synergism was related to the hydrogen spillover effect that was previously observed in HDT reactions over transition metal sulphides [48–51].

For the first time the effect of hydrogen atoms migration from the metal particles to the support and over it was described in 1969. Boudart et al. called this effect as “spillover”, because hydrogen atoms spill over from a hydrogen-rich to a hydrogen-poor surface [52]. Hydrogen spillover effect in HDT reactions is usually investigated in stacked bed reactor with separated layers of the catalysts [48,49,53–57]. It has already been shown that cobalt sulphide can play the role of spillover hydrogen donor, whereas  $\text{MoS}_2$  – that of acceptor [41,48–50,58]. However, the influence of spillover effect on action of promoted CoMo sites has not been investigated yet. The objective of the research was to investigate the effect of the modifying alumina surface with cobalt sulphide on the physicochemical characteristics of the CoMoS active phase formed from  $\text{Co}_2\text{Mo}_{10}\text{HPA}$  as well as catalytic properties of the  $\text{Co}_2\text{Mo}_{10}/\text{Co}_x/\text{Al}_2\text{O}_3$  catalysts. Moreover, the role of cobalt sulphide particles on the surface of alumina supported CoMo-catalysts and the assumption about hydrogen spillover over catalyst surface from cobalt sulphide particles to CoMoS phase crystallites were studied.

## 2. Experimental

### 2.1. Supports and catalysts preparation

Commercial sample of alumina (from Novokuibyshevsk Catalyst Factory, specific surface area (SSA)  $220\text{ m}^2/\text{g}$ , pore volume  $0.74\text{ cm}^3/\text{g}$ , effective pore radius  $31.5\text{ \AA}$ ) was used in this work.

Co-modified carriers  $\text{Co}_x/\text{Al}_2\text{O}_3$ , where  $x$  (over the 0–10.0 wt.% range) is the Co-loading, were prepared by wetness impregnation of commercial alumina with Co (II) nitrate aqueous solutions. The impregnated samples were dried at 60, 80, and  $110\text{ }^\circ\text{C}$  (for 2 h at each temperature) and sulphided at  $400\text{ }^\circ\text{C}$  (2 h) in  $\text{H}_2\text{S}/\text{H}_2$  atmosphere (15 vol.%  $\text{H}_2\text{S}$ , flow rate is  $4.0\text{ L/h}$ ).

Ammonium salt of decamolybdodicobaltate  $(\text{NH}_4)_6[\text{Co}_2\text{Mo}_{10}\text{O}_{38}\text{H}_4] \times 7\text{H}_2\text{O}$  ( $\text{Co}_2\text{Mo}_{10}\text{Am}$ ) was prepared in accordance with the published procedures [59]. To confirm the composition and structure of HPC its elemental analysis was performed and IR spectra are recorded according to Nikulshin et al. [60].

$\text{Co}_2\text{Mo}_{10}/\text{Co}_x/\text{Al}_2\text{O}_3$  catalysts were prepared by impregnation of modified carriers with aqueous solutions containing the required amounts of  $\text{Co}_2\text{Mo}_{10}\text{Am}$ . The calculated amount of Mo in the catalysts was 12.7 wt.%. The total amount of Co in the catalysts depended on the Co-loading in the  $\text{Co}_x/\text{Al}_2\text{O}_3$  supports used. Then impregnated samples were dried (60, 80, and  $110\text{ }^\circ\text{C}$  for 2 h) without further calcination.

### 2.2. Characterization of prepared samples

#### 2.2.1. Supports and catalysts textural properties

Textural characteristics of the prepared supports and catalysts were determined by nitrogen adsorption at  $77\text{ K}$  on a Quantochrome Autosorb-1 adsorption porosimeter. The SSA was calculated using the Brunauer–Emmett–Teller method at relative partial pressure  $P/P_0$  of 0.05–0.3. The total pore volume and pore size distribution were measured by a desorption curve using the Barret–Joyner–Halenda model at relative partial pressure  $P/P_0$  of 0.99. The samples were vacuum-dried before the adsorption measurement at  $350\text{ }^\circ\text{C}$  for 6 h at  $p < 10^{-1}\text{ Pa}$ .

#### 2.2.2. X-ray diffraction (XRD)

The X-ray diffraction (XRD) patterns were obtained on a ARLX'-TRA Powder Diffractometer with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54056\text{ \AA}$ ), 38 mA, 43 kV with a scanning speed of  $2^\circ/\text{min}$ . Powders were loaded on the glass disk by packing the samples into a cavity on this disk. Obtained diffractograms were analyzed using the standard JCPDS files.

#### 2.2.3. High resolution transmission electron microscopy (HRTEM)

HRTEM images of the  $\text{MoS}_2$  catalysts were obtained on a Tecnai G2 20 electron microscope with lattice-fringe resolution  $0.14\text{ nm}$  at accelerating voltage  $200\text{ kV}$ . The high resolution images of periodic structures were analyzed by the Fourier method. A local energy-dispersive X-ray analysis (EDAX) was carried out on an EDAX spectrometer fitted with a Si (Li) detector with resolution  $130\text{ eV}$ . The samples examined by HRTEM were prepared on a perforated carbon film mounted on a copper grid.

The average length of the slab ( $\bar{L}$ ) and the stacking degree ( $\bar{N}$ ) were calculated and averaged using the data obtained from 8 to 10 TEM micrographs (an equivalent of at least 400 crystallites) for each catalyst. The average length ( $\bar{L}$ ) approximately corresponds to the diagonal dimension of the observed  $\text{MoS}_2$  platelet. The dispersion of edge and corner Mo atoms (denoted as  $D$ ) was also calculated. In this calculation, it was assumed that  $\text{MoS}_2$  is a perfect hexagon in accordance with Kasztelan et al. [61]. The  $D$  value was statistically evaluated by dividing the number of Mo atoms at the edge surface by the total number of Mo atoms using the crystallite sizes determined from HRTEM:

$$D = \frac{\text{Mo}_E + \text{Mo}_C}{\text{Mo}_T} = \frac{\sum_{i=1..t} 6n_i - 6}{\sum_{i=1..t} 3n_i^2 - 3n_i + 1} \quad (1)$$

where,  $\text{Mo}_E$ ,  $\text{Mo}_C$  and  $\text{Mo}_T$  are numbers of Mo atoms located on edges, corners and total number, respectively, in average  $\text{MoS}_2$  crystallite (evaluated from HRTEM),  $n_i$  is the number of Mo atoms along one side of the  $\text{MoS}_2$  slab determined from its length and  $t$  is the total number of slabs in the TEM micrographs.

The average stacking degree ( $\bar{N}$ ) was calculated by the following equation:

$$\bar{N} = \frac{\sum_{i=1..t} n_i N_i}{\sum_{i=1..t} n} \quad (2)$$

where,  $n_i$  is the number of stacks in  $N_i$  layers.

#### 2.2.4. X-ray photoelectron spectroscopy (XPS)

The XPS spectra were obtained on a Kratos Axis Ultra DLD spectrometer using monochromatic  $\text{AlK}\alpha$  source ( $h\nu = 1486.6\text{ eV}$ ,  $150\text{ W}$ ). Analysis procedure described in details in [26,27]. CoMo/ $\text{Al}_2\text{O}_3$  spectra decomposition technique used in this work was developed by Gandubert et al. [62,63].

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