



# Effect of the second metal of Anderson type heteropolycompounds on hydrogenation and hydrodesulphurization properties of $\text{XMo}_6(\text{S})/\text{Al}_2\text{O}_3$ and $\text{Ni}_3\text{-XMo}_6(\text{S})/\text{Al}_2\text{O}_3$ catalysts

P.A. Nikulshin<sup>a</sup>, N.N. Tomina<sup>a</sup>, A.A. Pimerzin<sup>a</sup>, A.Yu. Stakheev<sup>b</sup>, I.S. Mashkovsky<sup>b</sup>, V.M. Kogan<sup>b,\*</sup>

<sup>a</sup> Samara State Technical University, 244, Molodogvardiyskaya st., Samara, 443100, Russia

<sup>b</sup> N.D. Zelinsky Institute of Organic Chemistry, RAS, 47, Leninsky prosp., Moscow, 119991, Russia

## ARTICLE INFO

### Article history:

Received 20 April 2010

Received in revised form

18 November 2010

Accepted 21 November 2010

Available online 27 November 2010

### Keywords:

Hydrotreatment

Catalysis

Heteropolycompounds

Diesel

Activity

Benzene

Thiophene

## ABSTRACT

The catalysts of the  $\text{XMo}_6(\text{S})/\text{Al}_2\text{O}_3$  and  $\text{Ni}_3\text{-XMo}_6(\text{S})/\text{Al}_2\text{O}_3$  structures were prepared from heteropolycompounds (HPCs) of Anderson type (where X = Co, Ni, Cr, Mn, Fe, Cu, Zn, Ga). The precursors and synthesized catalysts were characterized by FTIR, XRD, EXAFS, HRTEM techniques. The prepared catalysts were examined in model reactions of thiophene HDS and benzene HYD and in hydrotreating (HDT) of diesel fraction. The correlations between the catalytic activities in HDS and HYD and the heats of thiophene adsorption depending on the nature of the heteroatom prove that it plays an important role in the formation and behavior of the HYD and HDS active sites. It was found that heteropolycompounds are effective precursors of a multilayered active phase of hydrotreating catalysts.

© 2010 Elsevier B.V. All rights reserved.

## 1. Introduction

Using HPCs instead of commonly used precursors for the preparation of HDT catalysts opens new prospects for raising their catalytic activity. In the mid-1980s, attempts to use HPCs as precursors for HDT catalysts were mainly focused on the application of HPCs of Keggin's type [1–19]. Later on, HPCs of Anderson type attracted attention of researchers [20–28]. The main advantage of HPC of Anderson type is the presence of a 3d-metal (Ni and Co including) as a heteroatom in heteropolyanion [4,11,21,22,24,28,29]. Such a metal plays a role of a promoter in the formation of the catalyst active phase and its nature is extremely important for catalytic activity. HPCs of Anderson type are favourable for catalyst preparation because of even adsorption of HPCs on the surface of the carrier and because the HPCs adsorption is described by the Langmuir-type curve [20–22,24]. Besides, catalyst synthesis from HPC of Anderson type makes it possible to exclude calcining and, thus, to prevent  $\text{Co}(\text{Ni})\text{Al}_2\text{O}_4$  spinel formation [21–23]. The catalysts prepared in this way exhibit good reducing and sulphidizing properties [20,22,23].

So far studies have been mainly focused on the following compounds (anions):  $[\text{Ni}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{4-}$  ( $\text{NiMo}_6\text{HPC}$ ),  $[\text{Co}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{4-}$  ( $\text{CoMo}_6\text{HPC}$ ),  $[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{3-}$  ( $\text{AlMo}_6\text{HPC}$ ) and  $[\text{Rh}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{3-}$  [4,11,20–22,24,25,28,29]. The catalysts prepared with these HPCs were examined only in the model reaction of thiophene HDS but not in reactions with real oil fractions. Now Anderson type HPCs with X = Cr, Mn, Fe, Cu, Zn, Ga as precursors of HDT catalysts start attracting researchers' attention [13,30–36].

The purpose of this study is to investigate the influence of the second metal X of an HPC of Anderson type on the catalytic properties of  $\text{XMo}_6(\text{S})/\text{Al}_2\text{O}_3$  and  $\text{Ni}_3\text{-XMo}_6(\text{S})/\text{Al}_2\text{O}_3$  systems in HYD and HDS reactions of the model compounds (thiophene, benzene) and diesel fraction of oil.

## 2. Experimental

### 2.1. Synthesis of HPCs of Anderson type, catalysts

Ammonium salts of HPCs of Anderson type  $(\text{NH}_4)_{6-x}[\text{X}^x(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot n\text{H}_2\text{O}$  ( $\text{XMo}_6\text{HPC}$ ) with X = Cr (III), Mn (II), Fe (II), Ni (II), Co (II), Cu (II), Zn (II), Ga (III) were synthesized according to [36–38]. To confirm the structures of the synthesized HPCs their IR spectra were recorded with FTIR spectrometer

\* Corresponding author. Tel.: +7 499 1358774; fax: +7 499 1355328.  
E-mail address: [vmk@ioc.ac.ru](mailto:vmk@ioc.ac.ru) (V.M. Kogan).

Avatar 360. The phase compositions of the synthesized catalysts and the initial HPCs were determined using XRD method (X-ray diffractometer DRON-2 equipped with Cu-K $\alpha$ -anode detector) [39,40].

$\gamma$ -Al $_2$ O $_3$  with specific surface area 315 m $^2$ /g and effective pore diameter 110 Å was used as a carrier. The XMo $_6$ (S)/ $\gamma$ -Al $_2$ O $_3$  and Ni $_3$ -XMo $_6$ (S)/ $\gamma$ -Al $_2$ O $_3$  catalysts were prepared by wet impregnation of the carrier in HPC solution or by co-impregnation in HPC and Ni(NO $_3$ ) $_2$ ·6H $_2$ O solution with moisture capacity control. The co-solutions of Ni(NO $_3$ ) $_2$  and HPC were stable. The catalyst synthesized from (NH $_4$ ) $_6$ Mo $_7$ O $_{24}$ ·4H $_2$ O (ammonium heptamolybdate AHM chemically pure – c.p.) was taken as a reference. In the prepared catalysts the Mo and Ni contents were 10 wt.% and 2.9 wt.%, respectively.

The catalysts were treated by thermo-programmed stepwise drying from 80 to 120 °C with step of 20 °C (duration of one step was 2 h), so that total period of drying was 6 h. Then the temperature was raised up to 400 °C with heating rate 1 °C/min for further calcining for 2 h. Next the catalysts were subjected to sulphidation. A catalyst fraction of 0.25–0.50 mm was impregnated by a sulphidizing agent – ditert-butylpolysulphide (S content 54 wt.%) and placed into a separate glass reactor where sulphidizing process was carried out for 2 h at  $T = 400$  °C and H $_2$  pressure = 100 kPa.

## 2.2. Characterization of the catalysts

To confirm the structure of the heteropoly compounds, their IR spectra were recorded with an Avatar 360 (FTIR) instrument; the EXAFS spectra of Mo K-edge of the prepared catalysts and unsupported MoS $_2$  were recorded under the conventional transmission mode at the EXAFS Station of the Siberian Synchrotron Radiation Center (Novosibirsk) [41]. The storage ring VEPP-3 with the electron beam energy of 2 GeV and the average stored current of 100 mA was used as a source of radiation. The spectrometer had 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 a standard VIPER code [42]. The FEFF7 program was employed to fit the parameters of scattering [43].

HRTEM images of the catalysts were obtained on a Tecnai G2 20 electron microscope 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 (EDX) was carried out on an EDAX spectrometer (EDAX Co) fitted with a Si (Li) detector with a resolution of 130 eV. The samples examined by HRTEM were prepared on a perforated carbon film mounted on a copper grid.

## 2.3. Catalytic activity examination

### 2.3.1. Thiophene hydrodesulphurization

The catalytic activity of the samples was determined in a pulse microcatalytic reactor unit under a hydrogen gauge pressure of 0.25 atm in the thiophene hydrogenolysis reaction over the range of 300–400 °C with a step size of 20 °C. The mass of the catalyst sample was 25 mg and the thiophene volume was 0.2  $\mu$ l. The products were separated chromatographically on a fused-silica capillary column with the bonded OV-101 phase.

### 2.3.2. Benzene hydrogenation

The model structurally insensitive reaction of benzene hydrogenation was used for HYD activity testing ( $P_{H_2} = 2.0$  MPa, a reaction temperature range was between 300 and 460 °C, flow conditions). Catalyst loading was  $0.450 \pm 0.005$  g. Particle size was

0.25–0.5 mm. Hydrogen flow velocity was 40 cm $^3$ /min, benzene feed rate was 0.5 mL/h. Hydrogen and benzene were mixed in a mixer-evaporator. After that the benzene–hydrogen mixture was fed into the reactor. The products were injected through a 6-way valve-sampler equipped with a loop of 1  $\mu$ L into the GC installed at the outlet of the reactor. GC analysis was carried out using a stainless steel column filled with the sorbent containing 15% Carbowax 20 M on Chesosorb with graining of 0.25–0.36 mm. He was used as carrier gas. Cyclohexane and traces of methylcyclopentane (<1 wt.%) were detected in the products.

### 2.3.3. Hydrotreating of diesel fraction

The synthesized catalysts were tested in a bench-scale flow reactor unit in the process of hydrotreating mixture of light catalytically cracked gas oil and straight-run diesel in the ratio 1 to 1 by volume. The sulphur content of the feedstock was 1.090 wt.%, and the amount of polycyclic aromatic compounds (PACs) was 14.01 wt.%. The system contained units for specifying, maintaining, and controlling the temperature, pressure, and hydrogen-containing gas and feed flow rates. The reactor temperature, pressure, feed and hydrogen flow rates were maintained within  $\pm 2$  K,  $\pm 0.05$  MPa,  $\pm 0.1$  ml/h, and 0.2 l/h, respectively. The tests were performed under the following conditions: temperatures of 320, 340, 360, and 380 °C; pressure of 4.0 MPa; feed volume space velocity of 2.0 h $^{-1}$ ; hydrogen: feedstock ratio of 600 Ni/l; and catalyst volume of 10 cm $^3$ . The total sulphur content in the feed and hydrogenation products was determined on a Shimadzu EDX800HS analyzer. The concentrations of PACs were determined on a Shimadzu UV-1700 spectrophotometer.

Catalysts activity was determined by measuring the remaining amount of sulphur (**HDS**) and PACs (**HYD**) in hydrogenation products.

$$\text{HDS} = \frac{C_S^0 - C_S}{C_S^0} \quad (1)$$

where  $C_S^0$  – sulphur content in feedstock, 1.090 wt.%,  $C_S$  – sulphur content in hydrogenation products, wt.%.

$$\text{HYD} = \frac{C_{\text{PACs}}^0 - C_{\text{PACs}}}{C_{\text{PACs}}^0} \quad (2)$$

where  $C_{\text{PACs}}^0$  – PACs content in feedstock, 14.01 wt.%,  $C_{\text{PACs}}$  – PACs content in hydrogenation products, wt.%.

## 3. Results and discussion

### 3.1. Physical–chemical properties of synthesized XMo $_6$ (S)/Al $_2$ O $_3$ and Ni $_3$ -XMo $_6$ (S)/Al $_2$ O $_3$ catalysts

IR spectra of the synthesized heteropolycompounds are shown in Fig. 1. The characteristic bands of the synthesized Anderson HPCs coincide with those described in the literature [23,44–47]. The intense absorption bands at 950–800 cm $^{-1}$  are attributed to the cis-MoO $_2$  bonds, and the bands at 650–450 cm $^{-1}$  correspond to the bridging Mo–O–Mo bonds. The X-ray diffraction data show that the obtained heteropolycompounds have a complex isomorphous crystal structure. The interplanar distances are consistent with the published data [48–50].

Chemical compositions of the prepared samples are given in Table 1. These samples were characterized by FTIR, XRD, EXAFS, HRTEM methods. The FTIR spectra of the synthesized catalysts in the oxide form have no characteristic band and a broadened line in the area of 500–1500 cm $^{-1}$  is typical for  $\gamma$ -Al $_2$ O $_3$ . The X-ray diffraction patterns demonstrate only low temperature phase of  $\gamma$ -Al $_2$ O $_3$  at  $d/n = 1.971$  Å and  $d/n = 1.401$  Å. The samples (in oxide and sulphide states) were 3D X-ray amorphous, i.e. the area of coherent

Download English Version:

<https://daneshyari.com/en/article/41751>

Download Persian Version:

<https://daneshyari.com/article/41751>

[Daneshyari.com](https://daneshyari.com)