



Investigation of co-promotion effect in NiCoMoS/Al₂O₃ catalysts based on Co₂Mo₁₀-heteropolyacid and nickel citrate



A.V. Mozhaev^a, P.A. Nikulshin^{a,*}, Al.A. Pimerzin^a, K.I. Maslakov^b, A.A. Pimerzin^a

^a Samara State Technical University, 244 Molodogvardiyskaya St., Samara 443100, Russia

^b Chemistry Department, M.V. Lomonosov Moscow State University, 1-3 Leninskiye Gory, Moscow 119991, Russia

ARTICLE INFO

Article history:

Received 28 March 2015

Received in revised form 15 October 2015

Accepted 4 November 2015

Available online 4 December 2015

Keywords:

CoMoS

NiCoMoS

Hydrodesulphurisation

Heteropolyanion

Citric acid

DBT

ABSTRACT

Ni(Co)_x-Co₂Mo₁₀/Al₂O₃ catalysts with various (Co+Ni)/(Co+Ni+Mo) atomic ratio (from 0.17 to 0.45) and constant Mo loading (10 wt.%) were synthesised using decamolybdodibocobaltate heteropolyacid (Co₂Mo₁₀HPA) and cobalt or nickel citrate. The catalysts were characterised using N₂ physisorption, high-resolution transmission electron microscopy and X-ray photoelectron spectroscopy and tested in the hydrodesulphurisation (HDS) of dibenzothiophene (DBT). It was found that adding the Co(Ni) citrate to Co₂Mo₁₀/Al₂O₃ catalyst significantly altered the active phase morphology. The average slab length increased from 3.0 to 4.1 nm in Co_x-Co₂Mo₁₀/Al₂O₃ catalysts and to 3.6 nm in Ni_x-Co₂Mo₁₀/Al₂O₃ counterparts. The average stacking number of the MoS₂ crystallites grew from 1.4 to 2.0 with loading the Co or Ni. Increasing the Co content in the Co_x-Co₂Mo₁₀/Al₂O₃ catalysts decreased the Co percentage in the CoMoS phase and led to the growth of Co fraction in cobalt sulphide. With the increase of Ni content in Ni_x-Co₂Mo₁₀/Al₂O₃ catalysts the Ni percentage in the NiCoMoS phase decreased from 47 to 25 rel.% and the Co percentage in the NiCoMoS phase was constant and equal to ~62 rel.%. For both series of the catalysts, activity in DBT HDS passed through maximum at 0.33 of the atomic ratio (Co+Ni)/(Co+Ni+Mo). Ni_x-Co₂Mo₁₀S/Al₂O₃ catalysts indicated higher rate constants in DBT HDS than Co_x-Co₂Mo₁₀S/Al₂O₃ counterparts at the same metal content. It was concluded that Ni₁-Co₂Mo₁₀/Al₂O₃ sample with minimal Ni/Mo ratio had mixed Ni-Co-Mo sites with high turnover frequencies values.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

The hydrotreating (HDT) of petroleum cuts and residues is the central refining process in the production of clean fuels that meets the actual ecological requirements [1]. The changing feedstock quality and involvement of unconventional hydrocarbon resources (oil shales, bituminous oils, bio-raw materials, etc.) into the hydroprocessing require the development of more active catalysts. Ni(Co)Mo(W)/Al₂O₃ catalysts are widely used for HDT of various crude oils. The catalytic synergy of these systems is provided by formation of a Ni(Co)MoS phase containing highly dispersed MoS₂ crystallites decorated with Ni or Co atoms that act as promoters [2]. The active phases of transition metal sulphide catalysts are usually classified as Type I and Type II. The Type II active phase is more active than the Type I because of its weaker interaction with the support and higher extent of sulphidation [2,3]. These active phases are obtained by sulphidation of an oxidic precursor prepared

through the incipient wetness impregnation method using γ -Al₂O₃ with an aqueous solution containing the elements to be deposited. Ammonium heptamolybdate and cobalt nitrate are used in conventional synthesis processes. Many different approaches have been proposed for improving the preparation of these Co(Ni)Mo oxidic precursors, such as using carriers with varying acidic properties, incorporating additives (including organic additives and chelating agents) into the impregnation solution or using new starting materials when preparing the impregnation solutions. Applying heteropolycompounds (HPCs) instead of the precursors commonly used to prepare HDT catalysts offers new opportunities for improving the catalysts' activity [4–13].

The catalytic properties are directly determined by the HPCs used to prepare the oxidic precursor. The main advantage of Anderson-type HPCs is that they contain a 3d metal (e.g., Ni or Co) in the heteropolyanion (HPA) [5–7]. This metal promotes the formation of the promoted active sites, and the nature of the promoter strongly affects the catalytic activity. Using HPAs with a higher Co/Mo ratio ([Co₂Mo₁₀O₃₈H₄]⁶⁻ (hereafter Co₂Mo₁₀HPA)) led to an enhanced promoting effect of the cobalt during thiophene hydrodesulphurisation (HDS) [5,6,8–13].

* Corresponding author. Tel.: +7 846 242 3580; fax: +7 846 242 3580.
E-mail address: P.A.Nikulshin@gmail.com (P.A. Nikulshin).

It is well known [1,2,7] that the type of promoter atoms significantly affects the activity of the MoS₂ based catalysts. Moreover, simultaneous using of both metals (Co and Ni) for catalyst preparation resulted in synergetic improving the performances of NiCoMoS/Al₂O₃ catalysts [14–17]. Lee et al. [14] reported that NiCoMo/γ-Al₂O₃ showed higher activities and enhanced maintenance in HDT of atmospheric residual oil than did a commercial CoMo/γ-Al₂O₃ catalyst. Ishida with co-workers [15] found that the trimetallic NiCoMo/Al₂O₃ catalyst exhibited the best performance in the dibenzothiophene (DBT) HDS than either NiMo or CoMo catalyst in the presence of either rich H₂S or rich NH₃ thanks to dual promoting effect of NiCoMo. Qian et al. [16] investigated a promotion effect of nickel on Co-Mo/Al₂O₃ catalyst in DBT HDS using a ³⁵S radioisotope tracer method. They concluded that Ni-promoted Co-Mo/Al₂O₃ catalysts with lower molar Ni/Mo ratio (ca. 0.3) had greater amount of labile sulphur and values of the rate constant of [³⁵S]H₂S release than Co-Mo/Al₂O₃ catalyst and resulted in higher HDS activity. This indicated that the addition of Ni to Co-Mo/Al₂O₃ catalyst enhanced the formation of the active sites, which may be more reactive than that on Co-Mo catalyst such as “NiMoS” phase, or “NiCoMoS” phase. It was concluded that number of these active sites was limited by two possible reasons. First, one atom of Ni should connect with near two atoms of Co to form “Ni-Co-Mo-S” phase. Second, CoMoS phase was already formed before the addition of Ni. On the other hand, the promoting effect of nickel to Mo/Al₂O₃ almost disappeared with the addition of cobalt into Ni-Mo/Al₂O₃ catalysts, suggesting that cobalt hindered the formation of more active Ni-Mo-S phase or covered it. Yin et al. [17] reported that the binary promoted NiCoMoS catalyst exhibited distinctly higher activity than NiMoS and CoMoS catalysts in DBT HDS. The bulk NiCoMoS catalyst was also efficient in the HDS of gas oil with high sulphur content, and it could drop the sulphur content from 12 180 to 7.5 ppm, quite lower than that on a reference NiMo/Al₂O₃ catalyst, there it was 135 ppm after HDS reaction. Despite of the positive effects of dual promotion, recently, Vrinat with co-workers [18] reported a lower catalytic activity for the CoNiMoS supported on Al₂O₃ or TiO₂ systems compared to the CoMoS and NiMoS in 4,6-dimethyldibenzothiophene HDS. The catalysts were prepared by so-called “acac” method consisting in promotion of supported MoS₂ solids with Co(Ni) acetylacetonate in contrast to conventional incipient wetness impregnation techniques [14–16]. The detailed characterization of the catalysts supported on Al₂O₃ and TiO₂ demonstrated that Co reacted faster with MoS₂ than Ni. A lower synergetic effect of CoNiMoS catalysts was certainly caused by a bad accessibility of the reactants to some of the CoMoS or NiMoS active sites, due to the presence of inactive species of second promoter. Thus, investigation of dual promotion in ternary NiCoMo sulphides is an indispensable task for designing of highly effective HDT catalysts.

Recently we found in our laboratory [19–21] that simultaneous using of Co₂Mo₁₀HPA and Co citrate complex as precursors led to formation of highly active Co₃-Co₂Mo₁₀/Al₂O₃ catalysts for deep diesel HDT which supported MoS₂ species fully decorated with Co atoms. Investigation of the genesis of the catalysts [21] allowed us to understand the mechanism of formation of active phase species with high amount of promoted active sites. This result was achieved due to sulphidation peculiarities of both supported precursors of Co₂Mo₁₀HPA and cobalt citrate. Taking into account these interesting results, we decided to extend such an approach to supported NiCoMoS catalysts. Thus, the aim of this work was to investigate the co-promotion effect in NiCoMoS/Al₂O₃ catalysts based on Co₂Mo₁₀-heteropolyacid and nickel citrate. The quality of the NiMoS and CoMoS active sites was evaluated by combination of XPS, elemental analysis, TEM statistics and catalytic activity in DBT HDS. The results of this study should provide a better

understanding of the catalysts' structure of ternary NiCoMo sulphides and their HDS performance.

2. Experimental

2.1. Catalyst preparation

Decamolybdodicobaltate heteropolyacid H₆[Co₂Mo₁₀O₃₈H₄] (named Co₂Mo₁₀H₄) was prepared in accordance with the previous report [6]. For catalyst preparation, γ-Al₂O₃ (Sasol Company, Germany, specific surface area 245 m²/g, pore volume 0.5 cm³/g and effective pore diameter 56 Å) was crushed and sieved to an average particle size of 0.25–0.5 mm. Co₂Mo₁₀HPA/Al₂O₃ catalyst was prepared by wet incipient pore-volume impregnation of the alumina with Co₂Mo₁₀HPA solution of required concentration. Co(Ni)_x-Co₂Mo₁₀HPA/Al₂O₃ catalysts, where “x” is stoichiometric coefficient of cobalt (nickel) with various (Co+Ni)/(Co+Ni+Mo) molar ratio (from 0.17 to 0.45) and constant Mo loading (10 wt.%), were prepared by wet incipient pore-volume impregnation of the alumina with aqueous solutions containing the required amounts of CoCO₃ or NiCO₃, Co₂Mo₁₀HPA and citric acid monohydrate. The preparation procedures were as follows. CoCO₃ or NiCO₃, citric acid (with Co(Ni)/citric acid molar ratio = 1:1) and Co₂Mo₁₀HPA were added to ion-exchanged water followed by heating up to 50 °C and stirring to prepare impregnation solutions. The alumina supports were immersed in the impregnation solutions. The resulting catalysts were air-dried at 110 °C for 5 h without calcination. Next, the catalysts were subjected to sulphidation.

A reference Mo/Al₂O₃ catalyst was prepared by wet incipient pore-volume impregnation of alumina with a solution (pH 9), obtained from the dissolution of ammonium heptamolybdate (NH₄)₆Mo₇O₂₄ × 4H₂O (p.a.) in aqueous solution of NH₄OH in appropriate concentration to obtain catalyst with 10 wt.% Mo. Subsequently, the catalyst was air-dried at 110 °C for 5 h and then heated to 500 °C at 1 °C/min and calcined for 2 h in static air.

To analyse the catalysts using physicochemical methods, the catalyst samples were activated by sulphidation. A mixture of dimethyldisulphide (DMDS, 2 wt.% of sulphur) and decane at 3.5 MPa was utilised in a stepwise procedure conducted over 10 h at 240 °C and 8 h at 340 °C. Elemental analysis (Mo, Co and Ni) was performed using an EDX800HS analyser, and the coke content was determined by quantitative oxidation to CO₂ followed by GC analysis (Table 1).

2.2. Characterisation of catalysts

2.2.1. Textural characteristics of the catalysts

The textural characteristics of the prepared catalysts were determined by nitrogen adsorption performed at 77 K on a Quantochrome Autosorb-1 adsorption porosimeter. The SSA was calculated using the Brunauer–Emmett–Teller method at relative partial pressures (*P/P*₀) ranging from 0.05 to 0.3. The total pore volume (at *P/P*₀ of 0.99) and pore size distribution were calculated based on a desorption curve using the Barret–Joyner–Halenda model. Before the measurement, the samples were outgassed in vacuum better than 10⁻¹ Pa at 350 °C for 6 h.

2.2.2. High-resolution transmission electron microscopy (HRTEM)

HRTEM images of the catalysts were obtained on a Tecnai G2 20 electron microscope with a 0.14 nm lattice-fringe resolution and an accelerating voltage of 200 kV. The high-resolution images of the periodic structures were analysed using the Fourier method. Local energy-dispersive X-ray analysis (EDXA) was carried out on an EDXA spectrometer fitted with a Si (Li) detector with a 130 eV resolution. The samples used for HRTEM were prepared on a perforated

Download English Version:

<https://daneshyari.com/en/article/53522>

Download Persian Version:

<https://daneshyari.com/article/53522>

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