Journal of Catalysis 358 (2018) 155–167

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Efficient hydrodesulfurization catalysts derived from Strandberg P—Mo—Ni polyoxometalates

Jilei Liang [a,b], Mengmeng Wu [a,b], Pinghe Wei [b], Jinchong Zhao [a], Hua Huang [b], Cunfu Li [b], Yukun Lu [a,*], Yunqi Liu [a,*], Chenguang Liu [a,*]

[a] State Key Laboratory of Heavy Oil Processing, Key Laboratory of Catalysis of CNPC, China University of Petroleum (East China), Qingdao 266555, People's Republic of China
[b] Jiangsu Key Laboratory of Chiral Pharmaceuticals Biosynthesis, College of Pharmacy and Chemistry & Chemical Engineering, Taizhou University, Taizhou 225300, People's Republic of China

ARTICLE INFO

Article history:
Received 16 September 2017
Revised 22 November 2017
Accepted 24 November 2017
Available online 23 December 2017

Keywords:
Hydrodesulfurization
Sulfidation behavior
Strandberg polyoxometalates
Catalyst precursor
Molecular approach

ABSTRACT

Highly active hydrodesulfurization (HDS) catalysts have been prepared successfully through a molecular approach using well-defined Strandberg P—Mo—Ni polyoxometalates (POMs) as superior precursors. The hand-picked POMs significantly facilitated not only the formation of highly dispersed Ni—Mo species but also the formation of abundant and accessible NiMoS active sites at lower sulfidation temperatures, thereby resulting in a remarkable activity improvement in comparison with reference catalysts prepared with conventional precursors. Characterization results revealed the multidirecting effects of the POMs component and structure on the morphology and composition of the species in the NiMoS active phase and the evolution of precursors during the catalyst preparation simultaneously. The bottom-up POMs-based preparation methodology provides a better understanding of HDS catalyst structure and performance, thus further shedding light on the rational design and controllable fabrication of efficient HDS catalysts.

1. Introduction

Because of the exhaustion of oil resources and the stiffening of environmental regulations, the production of sulfur-free fuels has recently become one of the most important problems in the petroleum refinery. Hydrodesulfurization (HDS) is the most effective process for removing refractory sulfur-containing molecules, such as dibenzothiophene (DBT), from petroleum-derived fuels [1–6]. Owing to the growing use of inferior feedstocks (bituminous oils, oil shales, bio-raw materials, etc.) and the increase of the depth of petroleum refining, the hydrotreating process needs significant improvement in the performance of HDS catalysts, spurring comprehensive research both in industry and academia. Today most industrial HDS catalysts are based on supported transition-metal sulfides, such as Ni—Mo/γ-Al_2O_3, in which the active phase is a binary synergistic NiMoS phase, consisting of two-dimensional well-dispersed nanolayers of MoS_2 decorated with Ni promoters at their edges according to the Topsoe model [7]. HDS catalysts are conventionally prepared by simultaneous or successive steps with little control over the metal–support interaction: Incipient wetness impregnation, followed by drying and calcination to produce oxidic catalysts, and subsequent activation by sulfidation. Generally speaking, the impregnation is the most crucial step, because the deposition of the oxidic precursor can influence the final formation of the NiMoS active phase [6,8–10].

Although these Ni-promoted MoS_2 catalysts exhibit great HDS activity improvement, optimizing and modifying the properties of MoS_2-based catalysts still face two challenges. The first challenge is the incomplete sulfidation and lower stacking of the active phase due to the formation of MoO_xS_y and amorphous MoO_3 phases, probably as a result of strong chemical interactions between the metal sulfide and support [11,12]. During the impregnation, the metal complexes, notably heteropolyanions, can interact strongly with unsaturated Al sites, leading to the formation of Al—O—Mo linkages after calcination, resulting in maldistribution of the oxidic Mo phase, such as $Al_2(MoO_4)_3$ and bulk MoO_3. These species are hard to sulfide and yield a type I NiMoS active phase with lower activity. The second problem lies in the control and tunability of the structure, size, and morphology of MoS_2 nanoslabs on alumina support [13,14]. It has been proved that the catalytic synergism of NiMo/Al_2O_3 catalysts can be attributed to the "secondary support" role of MoS_2 slabs for Ni species. The good dispersion and favorable size and morphology of supported Mo species can effectively promote the formation of more NiMoS bimetallic active sites. In addition,

---

* Corresponding authors.
E-mail addresses: lyk@upc.edu.cn (Y. Lu), liuyq@upc.edu.cn (Y. Liu), cgliu@upc.edu.cn (C. Liu).

https://doi.org/10.1016/j.jcat.2017.11.026

the formation mechanism, the microstructure, and the structure–activity relationship of the NiMoS active phase are not yet clarified in detail [15–18]. Thus, it is necessary to explore innovative synthetic routes with full molecular control of the active phase beyond conventional precursors.

To overcome the shortcomings of the conventional impregnation preparation, various methods have been tried to design and prepare more active Ni—Mo catalysts, such as employing chemical vapor deposition [19], modifying the alumina support [20,21], using noncomplexing inorganic and organic additives [22–24], and using novel chemical composition precursors [25–27], including Mo-containing polyoxometalates (POMs). The introduction of POMs in the preparation of HDS catalysts offers a new opportunity for improving the catalyst performance. The P—Mo impregnating solution is essentially a POMs-based system, including $P_2Mo_5O_{23}^{6-}$, $PMo_{12}O_{40}^{3-}$, $P_2Mo_{18}O_{62}^{6-}$, $PMo_9O_{31}(OH)_3^{6-}$, and $PMo_{11}O_{39}^{7-}$ [28]. These nanosized POMs clusters display a high negative charge, which can easily combine with almost all transition-metal elements and main-group nonmetal cations, naturally including Ni(Co) and P promoters, indicating that POMs can be used as potential molecular platform for the design and preparation of a multimetallic HDS active phase. More importantly, three main advantages of this preparation methodology are attributed to the POMs precursor, so-called “killing three birds with one stone”: (1) The association of Ni, Mo, and P sources at the molecular level ensures oxidic precursor preparation in a single impregnation step; (2) the desired homogeneous spatial distribution coupled with intimate interaction between key elements on the atomic scale efficiently guarantee the catalytic synergism of Ni and Mo in the final sulfided catalysts; (3) the well-defined crystal and molecular structure provide an ideal model for clarifying the transformation process and formation mechanism of NiMoS active phases. Hence, readily available water-soluble Keggin [29–31], Evans-Showell ($Co_2Mo_{10}O_{38}H_4^{6-}$) [15,32,33], and Anderson-type [16,34,35] POMs have been widely investigated, and they have led to a great enhancement of HDS performances compared with conventional precursors. Furthermore, several modifications have been explored to fabricate more efficient catalysts, such as reduced POMs [36] or cationic exchange to increase the Ni/Mo ratio [37,38] and the simultaneous use of POMs and Ni-chelating agents [15,22,23,31].

In our previous study, inspired by the self-assembly strategy in POMs chemistry, we first selected rational organic ligands to induce clusters in the impregnating solution and form novel layered Ni—Mo—O POMs and then successfully explored them as efficient precursors for HDS catalysts [39]. Furthermore, we derived highly dispersed Ni—Mo catalysts from the Waugh-type POMs precursors for the first time [40]. These results demonstrated that Ni—Mo bimetallic POMs can be efficient precursors for hydrotreating catalysts with high performance. Following up on our recent studies on HDS catalysts, we propose a novel strategy for rational design and controllable fabrication of Ni-promoted MoS_2 nanocrystallites employing special Strandberg POMs $[H_2P_2Mo_5O_{21}]^{4-}$ (denoted as P_2Mo_5) as precursors. It has been proved that the P_2Mo_5 structure is an essential component of the impregnating solution [1], but research on P_2Mo_5-based HDS catalysts has scarcely been touched. The excellent structural characteristics of P_2Mo_5 have also attracted our attention.

P_2Mo_5 is a very appealing precursor candidate, as shown in Fig. 1. It has (1) the smallest size (9.0 × 5.6 Å) among P—Mo POMs; (2) a nearly planar {Mo_5} ring structure with protection by two PO_3H capped units; (3) suitable location of the cation at the edge sites of the {Mo_5} plane; (4) the ability of one heteropolyanion to incorporate two Ni^{2+} cations to form a Ni—Mo—P—O cluster without foreign counterions, leading to a high Ni/Mo ratio of 0.4.

The objective of this work was to employ well-defined Strandberg P—Mo—Ni POMs as precursors for efficient HDS catalysts and to investigate the directing effect of POMs on the morphology and composition of the NiMoS active phase and hence on the catalytic activities, as well as to follow the simultaneous evolution of precursors from the NiMoO cluster to the NiMoS active phase during the sulfidation. The title materials were fully characterized at each step by a multitechnique approach, and they exhibited well-dispersed, size-controllable, suitably stacked, and easily sulfided HDS catalysts, which is a direct consequence of the POMs-based preparation methodology and provides a significant improvement of catalytic performance over conventional catalysts. The bottom-up molecular approach thus opens new avenues to understanding the mechanism of active phase species formation and the evolution of POMs during the preparation of catalysts.

2. Experimental

2.1. Preparation of the Strandberg P—Mo—Ni polyoxometalates

The P_2Mo_5 complex was prepared by the method proposed by Kwak et al. [41]. Ammonia (7 ml, 105 mmol) was added to a 70 ml solution containing phosphite (4.1 g, 50 mmol). After the solution had been boiled for half an hour, molybdic oxide (14.4 g, 100 mmol) was added to the solution and heated for 1 h. After cooling, the solution was filtered and evaporated, and $(NH_4)_4P_2Mo_5$ bulk powder was obtained. The reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. All reagents were used without further purification, and deionized water was employed in the experiments.

To confirm the crystallographic structure and composition of the POMs, many characterizations, such as powder X-ray diffraction (XRD), single-crystal XRD, X-ray fluorescence (XRF), and Fourier transform infrared (FT-IR) spectroscopy were performed.

Strandberg P—Mo—Ni POM $Ni(NH_4)_2[(HPO_3)_2Mo_5O_{15}]$ (hereafter $Ni(NH_4)_2P_2Mo_5$) and $Ni_2[(HPO_3)_2Mo_5O_{15}]$ (hereafter $Ni_2P_2Mo_5$) complexes were obtained by cation exchange. First, $Ba_{3/2}PMo_{12}O_{40}$ was obtained via the neutralization of $H_3PMo_{12}O_{40}$ with $Ba(OH)_2$. Then, $Ni_{3/2}PMo_{12}O_{40}$ was prepared by adding $NiSO_4$ according to the following equation:

$$3/2\ NiSO_4 + Ba_{3/2}PMo_{12}O_{40} \rightarrow 3/2\ BaSO_4 \downarrow + Ni_{3/2}PMo_{12}O_{40} \quad (1)$$

Finally, the cation exchange was carried out according to the equations

$$(NH_4)_4[(HPO_3)_2Mo_5O_{15}] + 2/3\ Ni_{3/2}PMo_{12}O_{40} \rightarrow Ni(NH_4)_2[(HPO_3)_2Mo_5O_{15}] + 2/3\ (NH_4)_3PMo_{12}O_{40} \downarrow \quad (2)$$

$$(NH_4)_4[(HPO_3)_2Mo_5O_{15}] + 4/3\ Ni_{3/2}PMo_{12}O_{40} \rightarrow Ni_2[(HPO_3)_2Mo_5O_{15}] + 4/3\ (NH_4)_3PMo_{12}O_{40} \downarrow \quad (3)$$

and $Ni(NH_4)_2P_2Mo_5$ or $Ni_2P_2Mo_5$ was prepared.

2.2. Catalyst preparation

Catalysts with Strandberg P—Mo—Ni POMs as precursors were prepared by incipient wetness impregnation of commercial γ-Al_2O_3 (Shandong Alumina Plant, People’s Republic of China). The impregnating solution contained the appropriate amount of $Ni(NH_4)_2P_2Mo_5$ or $Ni_2P_2Mo_5$, for the preparation of catalysts with 12 wt.% MoO_3. The resulting catalysts were dried at 120 °C overnight without calcination. The uncalcined catalyst using Mo—Ni POMs as precursors will lead to a greater number of promoted NiMoS sites during the sulfidation [36]. The as-prepared catalysts were denoted as $Ni(NH_4)_2P_2Mo_5/Al_2O_3$ and $Ni_2P_2Mo_5/Al_2O_3$, respectively. Reference catalysts with the same Ni, Mo, and P content as $Ni(NH_4)_2P_2Mo_5/Al_2O_3$ and $Ni_2P_2Mo_5/Al_2O_3$ (denoted as