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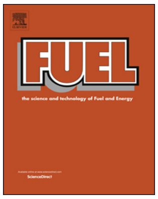


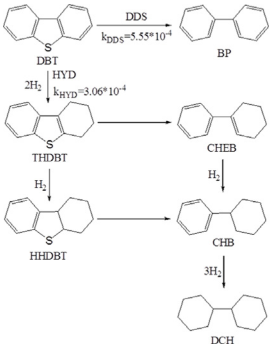
Full Length Article

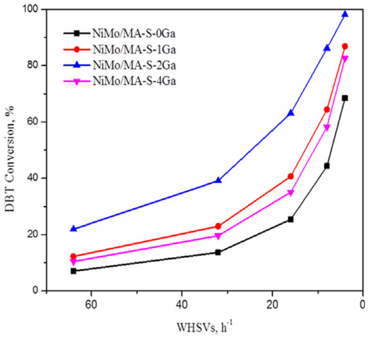
Effects of gallium addition to mesoporous alumina by impregnation on dibenzothiophene hydrodesulfurization performances of the corresponding NiMo supported catalysts

Wenwu Zhou[a,1], Yanan Zhang[b,1], Xiujuan Tao[c], Yasong Zhou[a,*], Qiang Wei[a], Sijia Ding[a]

[a] *State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing 102249, PR China*
[b] *CNOOC Central Laboratory (Shanghai), CNOOC EnerTech-Drilling & Production Co., Shanghai 200941, PR China*
[c] *College of Chemistry and Chemical Engineering, Shaanxi University of Science and Technology, Xi'an 710021, PR China*

GRAPHICAL ABSTRACT





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ABSTRACT

The effects of gallium (Ga) modification on mesoporous Al_2O_3 (MA) were studied, focusing on the morphology changes of the active phases and the application as catalyst support for catalytic performances for dibenzothiophene (DBT) hydrodesulfurization (HDS). MA samples with wide mesopore size distribution (MA-W), double mesopore size distribution (MA-D) and single mesopore size distribution (MA-S) were synthesized from the boehmite sol–gel via a hydrothermal synthesis method. The synthesized MA-S sample was modified with Ga_2O_3, and the corresponding sulfide NiMo supported catalysts were prepared. The as-synthesized samples were characterized by XRD, N_2 physisorption, NH_3-TPD, H_2-TPR, HRTEM and XPS. Superior catalytic performance was observed over the NiMo/MA-S-2Ga catalyst due to the moderate interaction between the active metals and the supports; the superior morphology for Ni promoted MoS_2 crystals, the highest sulfidation degree, the largest proportion of the NiMoS phase and the enhanced hydrogenation activity caused by the introduction of Ga species.

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[*] Corresponding author.
E-mail address: Zhys01@cup.edu.cn (Y. Zhou).
[1] Wenwu Zhou and Yanan Zhang contributed equally to this work.

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1. Introduction

The complete reduction of sulfur in fuel products to avoid the negative impacts caused by their combustion on both human health and the environment is still a topic of interest from scientists all over the world due to the stringent specifications established by governments [1,2]. It is now strictly limited below 10 ppm in major oil consumption areas, thus it is inevitable to remove the sulfur atoms from highly refractory organosulfur compounds such as dibenzothiophene (DBT) to reach such low sulfur contents [3,4]. Hydrodesulfurization (HDS) is considered to be among both the most effective and the most widely used techniques for the reduction of organosulfur compounds in the oil refining industries [5–7]. Design and development of HDS catalysts with high activity and selectivity is believed to be the key point of the HDS technique [8].

Supported MoS_2 promoted by Ni or Co hydrotreating catalysts is among the most commonly used catalysts in producing ultra-low sulfur diesel or so-called sulfur free diesel fuels [9]. γ-$A1_2O_3$ is the most widely used support materials for HDS catalysts due to its reasonably high surface area and ability to be formed into desired shapes with high mechanical strength and outstanding hydrothermal stability. However, the lack of ordered mesopores make it difficult to fully understand the effect of Ga modification on both the physicochemical properties and catalytic performances of the corresponding hydrotreating catalysts [10,11]. Our previous study [12] showed that the mass diffusion of compounds such as DBT can be eliminated only when the diameter of the mesopores is bigger than 4 nm. Therefore, one aim of this study is to synthesize mesoporous alumina with appropriate mesopore structures as excellent candidates for DBT HDS catalysts.

The edge and corner sites at the MoS_2 particles doped with Ni or Co atoms, namely the so-called Ni(Co)MoS active phase, are considered as the actual active phases of this kind of catalyst in the literatures [5,13–15], and there are already many studies focused on the structure and properties of active components [16–18]. It was reported that the Typ II NiMoS phase, which is considered to be more active than the Type I NiMoS phase because of its weaker interaction with the support materials and its higher sulfidation degree [16], with NiO/(NiO + MoO_3) = 1:3–1:4(mass ratio) was the most active [19]. At present, there have been many methods developed for the controlled synthesis of highly active HDS catalysts with certain NiMoS structures [16,20–22]. Recently, Haandel and coworkers [23] employed citric acid and phosphoric acid as chelating and non-chelating additives during the preparation of $CoMo/Al_2O_3$ catalysts with high HDS activities and high metal sulfidation degrees. Their systematical study showed that organic chelating agents can improve the correlation between the Mo species and the promoters. Other organic chelating agents, such as nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA) and tartaric acid (TA) [24] have also been reported to be used in the preparation of HDS catalysts with high metal dispersions, high sulfidation degrees and high HDS activities in the literatures. In summary, the use of organic chelating agents can promote the formation of weak complexes between the main metal atoms and the promoter metal atoms, which can be easily sulfided to form more highly active Type II NiMoS phase. Preparation methods have also been considered as an important factor in fabricating the highly active Type II NiMoS phase over the catalyst supports. Alsalme et al. [25] prepared a highly efficient NiMo supported HDS catalyst through Keggin polyoxometalate; they found that the catalysts they prepared exhibited faster sulfiding rates, superior HDS activity for thiophene and higher selectivity for butane. Xu and coauthors [26] reported a new method for preparing a highly efficient HDS catalyst by using gemini surfactant-dispersed Mo as precursor, according to the authors' description, the formation of highly dispersed MoS_2 crystals abundant with highly active edge and corner sites was facilitated. Recently, the doping of metal atoms such as Ir, Zn, Cu and Ga as a second promoter is considered another efficient strategy for preparing highly efficient HDS catalysts [27–31]. It is believed that adding such metal atoms can either improve the sulfidability of Ni and Mo precursors or promote more Ni atoms doping into MoS_2 crystals to form the real NiMoS active phase. Among all these metals, Ga is considered as the most promising one due to its chemical-physical similarity to the support materials. The effect of gallium on hydrodesulfurization catalysts has already been studied by several authors [32–35]. Altamirano and coauthors [31] found that the addition of Ga to the Al_2O_3 support modified the structural properties of NiMo and promoted the HDS efficiencies of both DBT and 4,6-DMDBT; similar findings was also made by Zepeda [36] and Díaz de León [37,38]. All these works explained this by proposing the theory that small amounts of Ga species could promote more Ni atoms doping into MoS_2 or WS_2 slabs to form more of the NiMo(W)S active phase. Similar findings were made in modifying HUSY zeolites by Ga as co-supports for the HDS catalyst in our previous works [22,39]. However, how Ga affects the morphology of active phase, how it affects the transformation of refractory organosulfur compounds such as DBT and whether gallium species exhibit HDS catalytic activity are still not clear.

Herein, in our present study, mesoporous Al_2O_3 samples with different mesopore structures were synthesized through the self-assembly of polyethylene glycol (PEG) and boehmite sol obtained from the hydrolysis of $Al(NO_3)\cdot 9H_2O$ and $Na[Al(OH)_4]$ at different temperatures. The typical physical properties of the investigated samples were analyzed via both small and wide-angle X-ray diffraction (XRD) analyses, N_2 physisorption and transmission electron microscopy (TEM) methods. The sample with single narrow dispersed mesopores (MA-S) was modified with different contents of Ga via the impregnation method, and the typical physical–chemical properties of the modified samples were analyzed by N_2 physisorption and NH_3 temperature-programmed desorption (NH_3-TPD) techniques. After being pelleted and crushed, the corresponding NiMo supported catalysts were prepared via an incipient wetness impregnation method. The typical chemical-physical properties of the catalysts were analyzed using H_2 temperature-programmed reduction (H_2-TPR), high resolution transmission electron microscopy (HRTEM) and X-ray photoelectron spectrometry (XPS) characterization methods. Finally, the HDS of DBT over the investigated catalysts were carried out and the effect of Ga modification on the transform of DBT molecules was discussed.

2. Experimental

2.1. Synthesis of materials

Mesoporous alumina samples with different mesopore structures were synthesized by the following procedure: 12.0 g of aluminum nitrate nonahydrate ($(Al(NO_3)_3 \cdot 9H2O$, Beijing Modern Oriental Fine Chemical Co. Ltd., ≥99.8%) was dissolved in 91.7 g of distilled water (0.33 M) in the reactor which was kept in a water bath of 50 °C. After it was completely dissolved, 15 g of PEG with an average molecular weight of 20,000 (PEG-20000) was added under continuous agitation (150 r/min). Simultaneously, 12.0 g of sodium aluminate ($Na[Al(OH)_4]$, Tianjin Guangfu Fine Chemical Co. Ltd., Ltd., ≥99.8%) was dissolved in 64.1 g of distilled water (1.5 M). After 10 min of agitation, the sodium aluminate solution was added to the reactor dropwise until the pH value of the solution rose to 9; 4 h later, the obtained white colloid was filtered and the solid product was washed by 30 mL of distilled water 3 times. Then, it was dried at 100 °C for 6 h and 120 °C for 3 h. After that, the obtained powder was calcined in a muffle furnace, where the temperature was programmed from room temperature to 550 °C with a heating rate of 3 $°C\cdot min^{-1}$ and then maintained for 4 h in air flow. The obtained sample was labeled MA-D. The sample synthesized by a similar procedure without adding PEG as the pore structure directing agent was labeled MA-W. Sample MA-S was also synthesized through a similar procedure, except the temperature of the water bath was set as 80 °C rather than 50 °C.