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Active sites of sulfided NiMo/Al_2O_3 catalysts for 4,6-dimethyldibenzothiophene hydrodesulfurization-effects of Ni and Mo components, sulfidation, citric acid and phosphate addition

Kentaro Kobayashi, Masatoshi Nagai*

Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan

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ABSTRACT

The active sites of the sulfided 5.2 wt%Ni9.8 wt%Mo/Al_2O_3 catalyst for the hydrodesulfurization of 4,6-dimethyldibenzothiophene were studied using a high-pressure flow system. The catalysts were prepared by dry sulfidation or after the calcination of four sets of NiMo precursors with and without citric acid and phosphoric acid. The dry sulfidation using the precursor of nickel carbonate and molybdenum trioxide with citric acid and phosphate produced the HDS MoO_3 is considered a precursor for the hydrogenation activity, and ammonium heptamolybdate is a precursor for the direct desulfurization activity. and the highest number of active sites of the $Ni^{2+}MoS_2$ slab (NiMoS phase) based on the NO and XPS. The sulfidation after calcination using nickel nitrate and ammonium hexamolybdate had the highest HDS rate for the desulfurization, and the number of sites of the MoS_2 (Mo^{4+}) slab covered with Ni sulfide (Ni^{2+}). This site was stacked with 3.3 layers and 34 Å length for the 2% phosphorus catalyst and widely dispersed as multilayers, and increased when stacked by the phosphate addition and contained highly stacked slabs by the citric acid addition.

1. Introduction

Recent environmental concerns have focused on an ultra-low sulfur transportation fuel which requires an extensive investigation to develop a highly-active catalyst, especially, a nickel (cobalt) containing molybdenum catalyst for hydrodesulfurization (HDS) in the petroleum chemistry field [1,2]. Stereotypically-hindered molecules among the most refractory sulfur-containing molecules in gas oils, such as 4,6-dimethyldibenzothiophene (DMDBT), are needed to reduce the sulfur content for use as a fuel. The mechanism with two active sites is well known for the HDS of dibenzothiophene on sulfided Mo/Al_2O_3 catalysts [3]; one site for the hydrogenation and the other site for the desulfurization. The catalysts have been extensively studied for their preparation, catalytic performance and characterization in order to obtain a highly-selective direct desulfurization. The active sites of the CoMo/Al_2O_3 catalyst are certainly understood, but for the NiMo/Al_2O_3 catalyst, they are still debated for the HDS of DMDBT. The formation of 3,3-dimethylbicyclohexyl (DMBCH) has been reported through three different pathways. First, DMBCH was formed from the hydrogenation of 3-methylcyclohexyltoluene (MCHT) formed through 4,6-dimethyltetrahydrodibenzothiophene (ThDBT) in one successive hydrogenation of DMDBT [4,5] or formed through DMBP produced from the direct desulfurization of DMDBT [6], while secondly, the DMBCH was formed from the undetected 4,6-dimethylperhydrodibenzothiophene produced through ThDBT [7,8]. Third, a pathway was proposed such that the DMBCH was formed from the simultaneous desulfurization and hydrogenation of DMDBT on the sulfided NiMo/Al_2O_3 catalyst [3]. This is based on the site-type analysis of the competitive adsorption of the sulfur and nitrogen compounds during the HDS of DMDBT. The third active site is present on the catalyst surface as well as the two active sites for the hydrogenation of DMDBT to MCHT and the direct desulfurization to DMBP. In this study, the three active sites based on the effects of nickel and molybdenum compounds, sulfidation process, chelating compounds and a phosphate compound on the surface properties, the activity and selectivity of the reaction product distribution during the HDS of DMDBT on the sulfided NiMo/Al_2O_3 catalyst are reported here.

The NiMo catalysts were prepared using four combinations of nickel and molybdenum compounds. The NiMo catalysts were prepared from nickel compounds, such as $Ni(OH)_2$ [9,10] and

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* Corresponding author.
E-mail address: mnagai@cc.tuat.ac.jp (M. Nagai).

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$NiCO_3$ [11], and molybdenum compounds, such as $MoO_3{\cdot}nH_2O$ [12] and nickel phosphomolybdate synthesized from nickel nitrate and phosphomolybdate [13] as well as the commonly prepared compounds of nickel nitrate hexahydrate and ammonium heptamolybdate. In this study, the NiMo catalyst was prepared with aqueous solutions of four sets of nickel and molybdenum compounds involving $Ni(OH)_2$, $Ni(NO_3)_2$ and $NiCO_3$, and $MoO_3{\cdot}nH_2O$ and $Mo(NH_4)_66(H_2O)$.

Sulfidation was carried out by the following two methods: The oxidic precursors were sulfided after calcination (calcination sulfidation) and sulfided by the elimination of the calcination (dry sulfidation) in order to avoid the decomposition of the complexes in the catalyst precursors. Moreover, the addition of a chelating ligand retards the sulfidation of the nickel cations while molybdenum is being fully sulfided. The dry sulfidation of NiMo catalysts with citric acid has been reported to provide the high activity for the HDS of thiophene and dibenzothiophene for the MoS_2/Al_2O_3 [14] and $MoS_2/MgO–Al_2O_3$ [15] and MoS_2/SBA-15 catalyst *s* [16]. The use of citric acid [14,16] was reported to produce smaller MoS_2 crystallites without altering the stacking and a greater number of $NiMo/SiO_2/Al_2O_3$ active sites [17]. The dry sulfidation of the CoMo oxidic precursor using citric acid was more highly effective than the pre-calcination or the absence of citric acid [18] due to the formation of the CoMoS II phase [19,20]. The calcination sulfidation, in contrast, has been studied to increase the sulfidation degree and hydrogenation activity, however, some difference in selectivity was observed using the dry sulfidation and calcination sulfidation of the NiMo catalyst [21]. Therefore, the sulfidation without or after calcination has been studied for two sets of Ni and Mo compounds with and without citric acid and phosphorus.

The other chelating ligands, such as ethylene glycol, triethylene glycol, nitrilotriacetic acid and ethylendiaminetetetraacetic acid, have been reported for the preparation of the NiMo catalyst using nickel nitrate, ammonium hexamolybdate [22] and molybdenum trioxide [11,12,16] by dry sulfidation. The chelating ligands increase the mobility of the nickel in the support so that the promoter can more easily react theMoS_2 phase by weakening the nickel-support interactions, thus favoring the formation of the catalytically-active Ni-Mo-S phase [23]. Thus, these ligands are effective for the formation of the catalytically-active NiMoS phase [19,24,25]. *trans*-1,2-Cyclohexadiamine- N,N,N′,N′-tetraacetic acid (CyDTA) was used [22,26] for the retardation of the sulfidation of nickel by increasing that of molybdenum leading to the NiMoS formation [26]. Thus, the effects of the addition of the three chelates of citric acid, CyDAT and ethylene glycol [27,28] to the $NiMo/Al_2O_3$ catalyst on the HDS activity and the citric acid addition on the surface properties and active sites were studied.

Phosphate has the beneficial effect of increasing the solubility of the molybdenum salts and the stability of the impregnation solution. The addition of phosphate has been studied concerning the improvement of the surface properties, such as the prevention of coking, increase in the distribution of the active species and the proper accumulation [29]. The coking on the surface of $NiMo/Al_2O_3$ was controlled by the phosphate addition due to the proper acidity on the surface. The phosphate addition caused the active metals to be stable in the impregnated solution [30] by providing a soluble molybdate phase by the formation of the phosphomolybdate of Mo and Ni with a high dispersion. The strong interaction of Ni metal with Al_2O_3 [31] changed the structural properties, which increased the dispersion and HDS activity of the $NiMo/Al_2O_3$ [32]. Furthermore, the multimolybdate $Al_2(MoO_4)_3$ crystal and MoO_3 were easily formed on the support with a small amount of phosphate [33,34], the multi-layer accumulation of MoS_2 by protection of the strong reaction of molybdenum with Al_2O_3 [35,36] and the strong bonding of Al_2O_3 with the phosphate [30,31]. In contrast, the large amount of phosphorus addition decreased the HDS activity. Thus, the good effect of the phosphate addition on the active sites of the $NiMo/Al_2O_3$ catalyst by sulfidation has been reported, but the effect of the sulfidation of the Ni and Mo precursors added with citric acid and phosphorus is not fully understood. The phosphoric acid is suitable for the addition to the catalyst prepared with $NiCO_3{\cdot}2Ni(OH)_2$ and MoO_3 [11]. Therefore, the formation of active species by phosphorus addition with and without citric acid during the dry and calcination sulfidations was studied based on XPS and TEM measurements.

Table 1
$NiMo/Al_2O_3$ catalysts prepared from nickel and molybdenum compounds.

Combination	Ni compound	Mo compound
A	$NiCO_3{\cdot}2Ni(OH)_24H_2O$	MoO_3
B	$Ni(OH)_2$	MoO_3
C	$NiNO_36H_2O$	$(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$
D	$NiCO_3{\cdot}2Ni(OH)_24H_2O$	$(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$

In this study, the $NiMo/Al_2O_3$ catalyst was prepared using four sets of nickel and molybdenum compounds, citric acid and two other chelates, the addition of 0–5.0 wt% phosphorus, and the subsequent dry and calcination sulfidations. The active sites of the sulfided $NiMo/Al_2O_3$ catalysts were studied based on the NO adsorption temperature-programmed reduction (TPR), XPS and TEM. The reaction mechanism for the HDS of DMDBT using a high-pressure flow system is discussed based on these results and a previous study of the site selective adsorption analysis.

2. Experimental

2.1. Catalyst preparation

2.1.1. NiMo metal oxide precursors supported on Al_2O_3

The NiMo precursors were prepared by the combination of compounds (A-D) using the mixtures of an aqueous solution of (A) nickel carbonate, $NiCO_3{\cdot}2Ni(OH)_2{\cdot}4H_2O$ and molybdenum trioxide, MoO_3, (B) nickel hydrate, $Ni(OH)_2$ and molybdenum trioxide, (C) nickel nitrate, $Ni(NO_3)_2{\cdot}6H_2O$ and ammonium hexamolybdate, $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, and (D) nickel carbonate and ammonium hexamolybdate. These are summarized in Table 1. The metal loadings were 5.2 wt% of NiO and 9.8 wt% of MoO_3 (molar ratio of Ni/Mo = 1) [37–39] with phosphoric acid (H_3PO_4). Each aqueous solution containing a molybdenum compound with phosphorus acid along with 1.0, 2.0 and 5.0 wt% phosphorus as P_2O_5 and another containing a nickel compound with a chelate (citric acid, ethylene glycol or *trans*-1,2-cyclohexadiamine-N,N,N′,N′-tetraacetic acid (CyDTA)) were separately stirred at 328 K (at 353 K for molybdenum trioxide) for about 2 h. The mixed solution was impregnated onto Al_2O_3 (Catalyst and Catalysis of Japan, JRC-ALO-3) by an incipient wetness method, then heated overnight at 393 K. The chelate had the atomic ratio of Ni/chelate of 1.2 for the citric acid and 0.6 for the CyDTA.

2.1.2. Sulfidation step by drying and calcination

The 1.0 g precursors of the NiMo supported alumina were packed into a fixed-bed microreactor and sulfided using two methods (drying with and without calcination). For the dry sulfidation method, the precursors contained compounds A-D with citric acid and 0, 1.0, 2.0 and 5.0% of phosphorus. In order to avoid the decomposition of the organic molecules and complexes, the precursors were heated at 393 K in a stream of dry air for 1 h and cooled to 323 K, sulfided from 323 to 443 K at 60 K/h in a stream of 10% H_2S/H_2 at 4 L/h, from 443 to 503 K at 30 K/h and from 503 to 623 K at 60 K/h, then kept at 623 K for 3 h. This catalyst will be expected to increase the formation of the NiMoS phase to prevent the sulfidation of nickel at low temperature. For the calcination sulfidation

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