# Modification of the alumina-supported Mo-based hydrodesulfurization catalysts by tungsten

Deuk Ki Lee [a,*] and Wang Lai Yoon [b]

[a] *Department of Environmental Engineering, Kwangju University, Kwangju 502-703, Korea*
[b] *Energy Conversion Research Team, Korea Institute of Energy Research, Taejon 305-343, Korea*

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The incorporation effect of tungsten as an activity-promotional modifier into the Ni-promoted Mo/$\gamma$-$Al_2O_3$ catalyst was studied. Series of W-incorporated catalysts with different content of tungsten were prepared by changing the impregnation order of nickel and tungsten onto a base Mo/$\gamma$-$Al_2O_3$. Catalytic activities were measured from the atmospheric reactions of thiophene hydrodesulfurization (HDS) and ethylene hydrogenation (HYD). The HDS and HYD activities of the WMo/$\gamma$-$Al_2O_3$ catalysts (WM series) initially increased and subsequently decreased with increasing content of tungsten as compared with those of their base Mo/$\gamma$-$Al_2O_3$. The maximal activity promotion occurred at the W/(W + Mo) atomic ratio 0.025. For the Ni-promoted Mo/$\gamma$-$Al_2O_3$ catalysts, the effect of W incorporation was greatly dependent on the impregnation order of tungsten. The catalysts prepared by impregnating Ni onto the WMo/$\gamma$-$Al_2O_3$ catalysts showed the same trend of activity promotion as for the WM series, while those by impregnating W onto a NiMo/$\gamma$-$Al_2O_3$ catalyst resulted in lower activities than their base NiMo/$\gamma$-$Al_2O_3$ catalyst. To characterize the catalysts, temperature-programmed reduction and low-temperature oxygen chemisorption were conducted. The effects of W incorporation on the NiMo-based catalysts were discussed in reference to those on the CoMo-based catalysts.

**Keywords:** hydrodesulfurization, Ni(Co)–Mo/$\gamma$-$Al_2O_3$ catalyst, tungsten incorporation, activity promotion

## 1. Introduction

Due to their great activity synergism in hydrodesulfurization (HDS) as well as in the other hydrotreating reactions, $\gamma$-$Al_2O_3$-supported CoMo and NiMo sulfide catalysts have been usually used for the HDS of petroleum oil fractions. However, regardless of their high intrinsic activity, these catalysts suffer from the severe deactivation problem during the hydroprocessing service, especially for the heavy oil feedstocks, mainly attributed to the rapid initial coking and the gradual decrease of active phase dispersion. It has been found [1,2] that the catalytic activity and the durability of a HDS catalyst are closely related to the dispersion of active phases over the support; the higher the active phase dispersion, the higher the catalytic activity and, simultaneously, the less the catalyst deactivation.

In order to increase the dispersion of active phases over the support and to stabilize the dispersed active phases, the modification of the supported catalysts with a metal additive as the second promoter has been employed in some studies. Migone and Meitzner [3] state that metals which remain in a high oxidation state under reducing conditions, when deposited on $Al_2O_3$, may disperse and stabilize the small active metal clusters. They also suggest that an effective metal modifier for a catalyst should strongly interact with the active metal clusters for their stabilization and, at the same time, should interact with the support for preventing its migration. However, as far as the catalytic system of the $Al_2O_3$-supported CoMo or NiMo is concerned, the metal modifier interacting with the active metals should not interfere with the formation of the active sulfide phases such as Co–Mo–S or Ni–Mo–S, because the high HDS activity of the catalysts is originated from such active synergy phases [4,5].

In a recent paper, Lee et al. [6] reported that the presence of an appropriate amount of tungsten in a NiMo/$\gamma$-$Al_2O_3$ catalyst brought about the beneficial effects on the catalyst performance in the high-pressure hydrotreating reactions of an atmospheric residual oil feed, i.e., enhanced sulfur conversion and lowered rate of initial deactivation. Subsequent series of publications [7,8] reported for the W-incorporated CoMo/$\gamma$-$Al_2O_3$ catalysts that the catalytic activity promotion was due to the presence of monomeric sulfidation-resistant $WO_3$ oxide species which played a role of increasing the dispersion of active Co–Mo–S phases over the support. Such a promotional role of the tungsten modifier in the CoMo/$\gamma$-$Al_2O_3$ catalyst system may be applied to the NiMo/$\gamma$-$Al_2O_3$ catalyst for the development of a NiMo-based catalyst of better reaction performance.

In this paper, we investigate the effects of tungsten addition to the Ni-promoted Mo/$\gamma$-$Al_2O_3$ catalyst on the catalytic activity by varying the content and order of tungsten impregnated and compare the catalytic behaviors of the W-incorporated NiMo/$\gamma$-$Al_2O_3$ with those of the W-incorporated CoMo/$\gamma$-$Al_2O_3$. Catalytic activities were measured from the atmospheric reactions of thiophene HDS and ethylene HYD. Temperature-programmed reduction (TPR) and low-temperature oxygen chemisorption (LTOC) were

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[*] To whom correspondence should be addressed.

Table 1
List of prepared catalysts.

| Notation[a] | W/(W + Mo) atomic ratio | Composition (wt%) NiO | $WO_3$ | $MoO_3$ | BET area ($m^2$/g) |
|---|---|---|---|---|---|
| Base catalysts | | | | | |
| Mo(4)/KHA | – | – | – | 13.3 | 115 |
| Ni(2.14)Mo(4)/KHA | – | 3.64 | – | 13.0 | 108 |
| WM series based on Mo(4)/KHA | | | | | |
| W(0.05)Mo(4) | 0.0125 | – | 0.25 | 12.8 | 110 |
| W(0.1)Mo(4) | 0.025 | – | 0.51 | 12.7 | 105 |
| W(0.21)Mo(4) | 0.05 | – | 1.08 | 12.6 | 105 |
| W(0.44)Mo(4) | 0.1 | – | 2.24 | 12.5 | 104 |
| W(1.0)Mo(4) | 0.2 | – | 4.93 | 12.2 | 99 |
| NWM series based on Mo(4)/KHA | | | | | |
| Ni(2.14)W(0.05)Mo(4) | 0.0125 | 3.58 | 0.27 | 12.8 | 104 |
| Ni(2.14)W(0.1)Mo(4) | 0.025 | 3.58 | 0.52 | 12.7 | 106 |
| Ni(2.14)W(0.21)Mo(4) | 0.05 | 3.56 | 1.06 | 12.6 | 94 |
| Ni(2.14)W(0.44)Mo(4) | 0.1 | 3.52 | 2.23 | 12.5 | 92 |
| Ni(2.14)W(1.0)Mo(4) | 0.2 | 3.41 | 4.90 | 12.2 | 91 |
| WNM series based on Mo(4)/KHA | | | | | |
| W(0.05)Ni(2.14)Mo(4) | 0.0125 | 3.57 | 0.28 | 12.8 | 105 |
| W(0.1)Ni(2.14)Mo(4) | 0.025 | 3.56 | 0.50 | 12.7 | 103 |
| W(0.21)Ni(2.14)Mo(4) | 0.05 | 3.55 | 1.09 | 12.7 | 100 |
| W(0.44)Ni(2.14)Mo(4) | 0.1 | 3.50 | 2.23 | 12.5 | 98 |
| W(1.0)Ni(2.14)Mo(4) | 0.2 | 3.42 | 4.91 | 12.2 | 94 |

[a] Numbers in parentheses following each catalytic metal indicate the number of metal atoms per square nm of $\gamma$-$Al_2O_3$ support.

used to characterize the catalysts in oxidic and sulfided states, respectively.

## 2. Experimental

### 2.1. Preparation of catalysts

The catalysts were prepared using the $\gamma$-$Al_2O_3$, Nishio KHA (surface area 150 $m^2$/g; pore volume 0.54 $cm^3$/g). Mo(4)/KHA was first prepared by incipient wetness impregnation of KHA with an aqueous solution of ammonium heptamolybdate tetrahydrate (Fluka, 99+%). The numbers in parentheses followed by each catalytic component indicate the number of atoms per square nm of support surface area. Ni(2.14)Mo(4)/KHA catalyst was prepared by impregnating the solution of nickel nitrate hexahydrate (Junsei, GR grade) on the Mo(4)/KHA. After the impregnation of each metal precursor, the catalyst was dried at 110 °C for 12 h and then calcined in dry air at 500 °C for 6 h as a routine preparation procedure. W-incorporated Mo(4)/KHA catalysts denoted WM series with different contents of tungsten were prepared by impregnating the solutions of ammonium metatungstate (Fluka, 97+%) on the Mo(4)/KHA catalyst. Two series of W–NiMo catalysts with different contents of tungsten were prepared varying the impregnation order of tungsten. Series of catalysts denoted NWM were made from the WM series catalysts by impregnating a fixed amount of nickel onto them. The other series of catalyst denoted WNM were obtained by the impregnation of tungsten onto the Ni(2.14)Mo(4)/KHA. The prepared catalysts are listed in table 1. When preparing tungsten-incorporated catalysts, the pH of the solution of ammonium metatungstate was adjusted to 9.5 by adding a diluted $NH_4OH$ solution. However, the pH of the impregnating solution of nickel nitrate or ammonium molybdate was not adjusted. The pH control of W-solution was based on the reports [9,10] that the monomeric species of tungsten anion $WO_4^{2-}$ predominated in alkaline solution of pH around 9.5. Metal compositions of the catalysts were determined by X-ray fluorescence (Aroma EX-6500) and BET surface areas were determined by nitrogen adsorption using a Quantachrome Autosorb-I. All the prepared catalysts were further crushed to particles of 100–300 mesh size before the use in experiments.

### 2.2. Measurement of catalytic activities

HDS and HYD activities of the catalysts were separately determined in a quartz U-shaped microreactor under atmospheric pressure using thiophene and ethylene as model compounds, respectively. Experimental details can be found elsewhere [7].

### 2.3. Catalyst characterization

Temperature-programmed reduction (TPR) and low-temperature oxygen chemisorption at 195 K were conducted for the catalyst samples in oxidic and sulfided states, respectively. Detailed experimental procedures can be found in [7,8].

## 3. Results

### 3.1. Catalytic activities

Figure 1 shows the relative reaction rates over the WM series catalysts in thiophene HDS and ethylene HYD when the reaction rate of their base Mo(4)/KHA catalyst in both reactions are regarded as unity. The measured reaction rate values of the base catalysts are listed in table 2. The WM series catalysts show the catalytic activity trend of an initial sharp increase and subsequent decrease with increasing content of tungsten as relative to their base Mo(4)/KHA catalyst. The activity promotion is maximized at the tungsten composition corresponding to 0.025 in W/(W + Mo) atomic ratio. It is also observed for the WM series catalysts that HYD reaction is more promoted than HDS.

Figure 2 shows the relative reaction rates over the NWM and WNM series catalysts in comparison with Ni(2.14)Mo(4)/KHA. As far as the NWM series catalysts are concerned, the catalytic activity behavior with the increasing content of tungsten is the same as that of WM series catalysts shown in figure 1. However, all the WNM series catalysts show lower activities than their base Ni(2.14) Mo(4)/KHA. It is assured that the activity promotion for the NiMo-based catalyst system is significantly dependent on the impregnation order of tungsten.

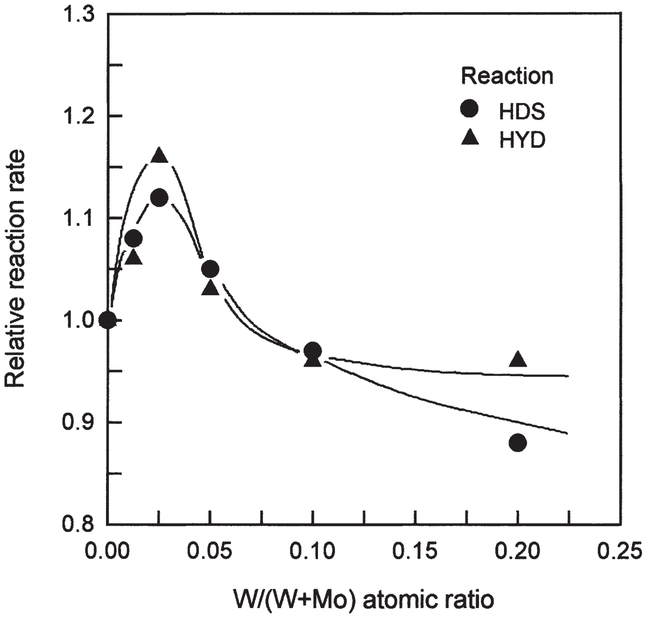

Figure 1. Reaction rates over WM series catalysts as relative to those over the Mo(4)/KHA.

Table 2
HDS and HYD reaction rates over some base catalysts.

| Catalysts | $r_{HDS}$ $\mu$mol thiophene converted $s^{-1}$ $g^{-1}$ at 350 °C | $r_{HYD}$ $\mu$mol ethylene converted $s^{-1}$ $g^{-1}$ at 275 °C |
|---|---|---|
| Mo(4)/KHA | 0.6 | 5.8 |
| Ni(2.14)Mo(4)/KHA | 2.6 | 6.4 |

### 3.2. Oxygen uptake

Oxygen uptakes of the sulfided catalysts as a function of tungsten content are shown in figure 3 for the WM, NWM and WNM series catalysts. It can be observed that the trends of oxygen uptake and those of activity behavior are quite similar to each other. For the alumina-supported Mo-based catalysts, coordinatively unsaturated sites (CUS)

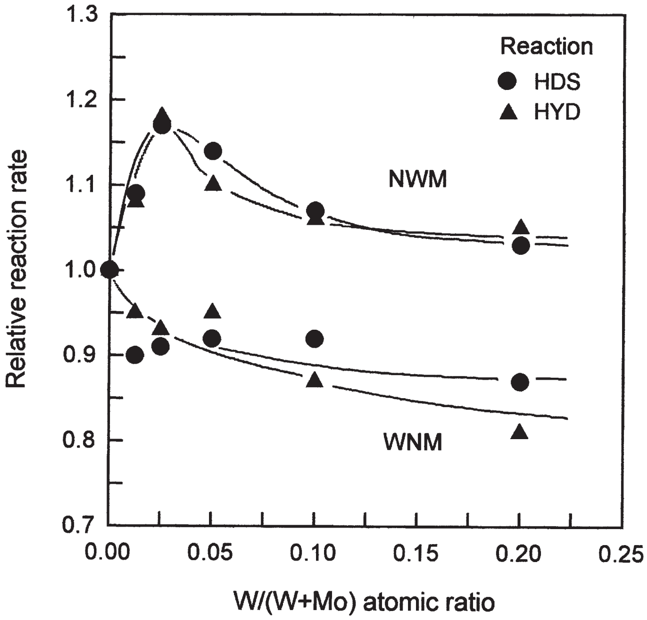

Figure 2. Reaction rates over NWM and WNM series catalysts as relative to those over the Ni(2.14)Mo(4)/KHA.

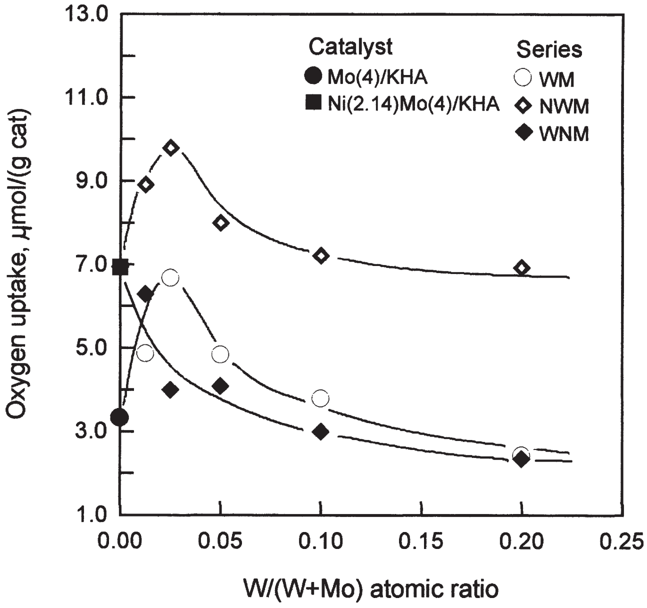

Figure 3. Oxygen uptakes of the sulfided WM, NWM and WNM series catalysts in comparison with the sulfided Mo(4)/KHA and Ni(2.14)Mo(4)/KHA.

or, in other words, anion vacancy sites on partially reduced and/or sulfided catalysts are generally accepted as the active sites where HDS, HYD and other hydroprocessing reactions take place. In order to measure the surface concentration of CUS and its correlation with catalytic activity, LTOC has been employed in a number of works [11–15]. It is also believed that, for sulfided catalysts, oxygen chemisorbs selectively and dissociatively on these CUS at temperatures around 195 K without attacking the bulk of the sulfide phase. Therefore, the results of oxygen chemisorption suggest that the presence of an adequate amount of tungsten in Mo/$\gamma$-$Al_2O_3$ and CoMo/$\gamma$-$Al_2O_3$ plays a role in facilitating the creation of CUS on the catalysts, but the excess amount of tungsten decreases the formation of CUS sites. It is also noted that the introduction of tungsten into a NiMo/$\gamma$-$Al_2O_3$ always leads to the decreased number of active sites on the catalyst.

### 3.3. Temperature-programmed reduction

Figure 4 shows the TPR profiles of Mo(4)/KHA and WM series catalysts. The TPR profile of the Mo(4)/KHA exhibits the two reduction regions with peak temperatures at around 448 and 700 °C, respectively. It has been proposed [16] that two Mo species are present for Mo loading up to monolayer coverage: (i) isolated tetrahedral molybdenum oxide ($Mo_t$), which is resistant to reduction, and (ii) ploymeric distorted octahedral molybdenum oxide ($Mo_o$), which is easier to be reduced. Several authors [16–19] suggested for the two-peak reduction pattern of Mo catalysts that the first low-temperature reduction peak is assigned to the partial reduction of $Mo_o$, while the second high-temperature peak to further reduction of such species plus that of $Mo_t$.

It is observed from figure 4 that the presence of a large amount of tungsten in the WM series catalysts decreases the area of the first reduction peak. In the catalysts such as W(0.44)Mo(4)/KHA and W(1.0)Mo(4)/KHA containing larger amounts of tungsten, a new reduction peak is observed at around 574 °C in conjunction with significant decrease in the first reduction peak area. This indicates that some of more reducible Mo oxide species have been transformed to a new species of less reducibility by the presence of a large amount of tungsten. However, for the catalyst W(1.0)Mo(4)/KHA of which W/(W + Mo) atomic ratio is as low as 0.025, an observable shift of the reduction peak towards lower temperature is present without a decrease in the peak area.

TPR profiles of NWM and WNM series catalysts are shown in figure 5 in comparison with their base Ni(2.14)Mo(4)/KHA. The TPR profiles of the promoted catalysts containing tungsten display two reduction peaks similar to those of their base NiMo catalyst. It is generally observed for these Ni-promoted, W-incorporated catalyst series that, as the incorporation content of tungsten increases, the width of the first reduction peak becomes broader and that the first reduction peak position is first shifted towards lower temperatures and then moved towards higher temperatures. However, the first peak position in the catalyst series WNM is shifted all through towards higher temperatures as the content of tungsten increases.

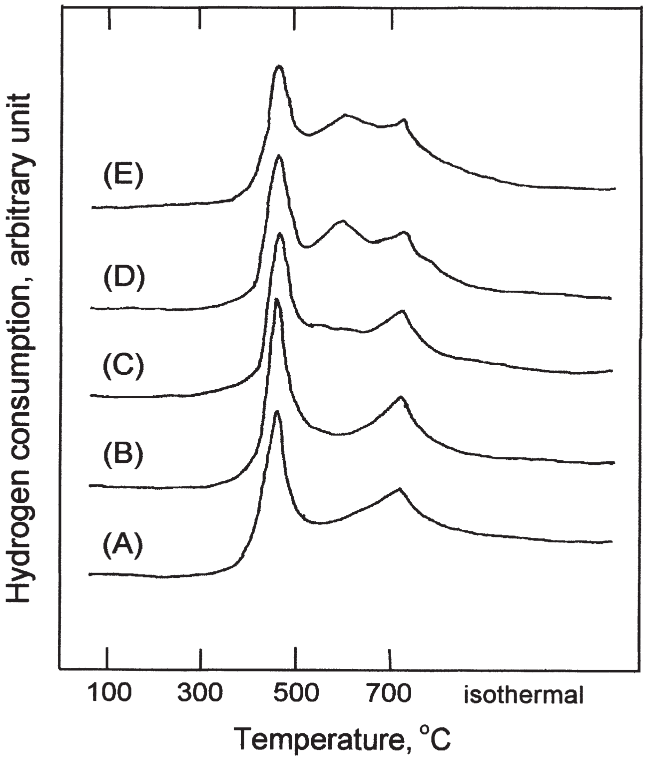

Figure 4. TPR profiles of Mo(4)/KHA (A) and the oxidic WM series catalysts with the W/(W + Mo) atomic ratios as follows: (B) 0.025, (C) 0.05, (D) 0.1, and (E) 0.2.

The shift of the first reduction peak towards lower temperatures suggests that some of the Mo species have been rendered more reducible by the presence of tungsten. This is observed for some W-incorporated catalysts containing a relatively low W content, of which catalytic activities appear to be promoted. The reduction peak width broadening towards higher temperatures observed in the relatively high W content catalysts indicates that the retardation occurred in the rate of reduction of the corresponding reducible species. Such effects of reduction retardation by tungsten appear not so large to be neglected in lower tungsten content, but become more and more significant with higher content of tungsten.

## 4. Discussion

In a previous study for the Co-promoted Mo/$\gamma$-$Al_2O_3$ catalyst, Lee et al. [8] reported that the catalytic activity promotion by W incorporation was predominatedly attributed to the role of sulfidation-resistant monomeric $WO_3$ species playing in dispersing the active phases during the catalyst sulfidation process. It was proposed that the dispersion increase proceeds through the concurrent split of larger patches of active phases into a larger number of

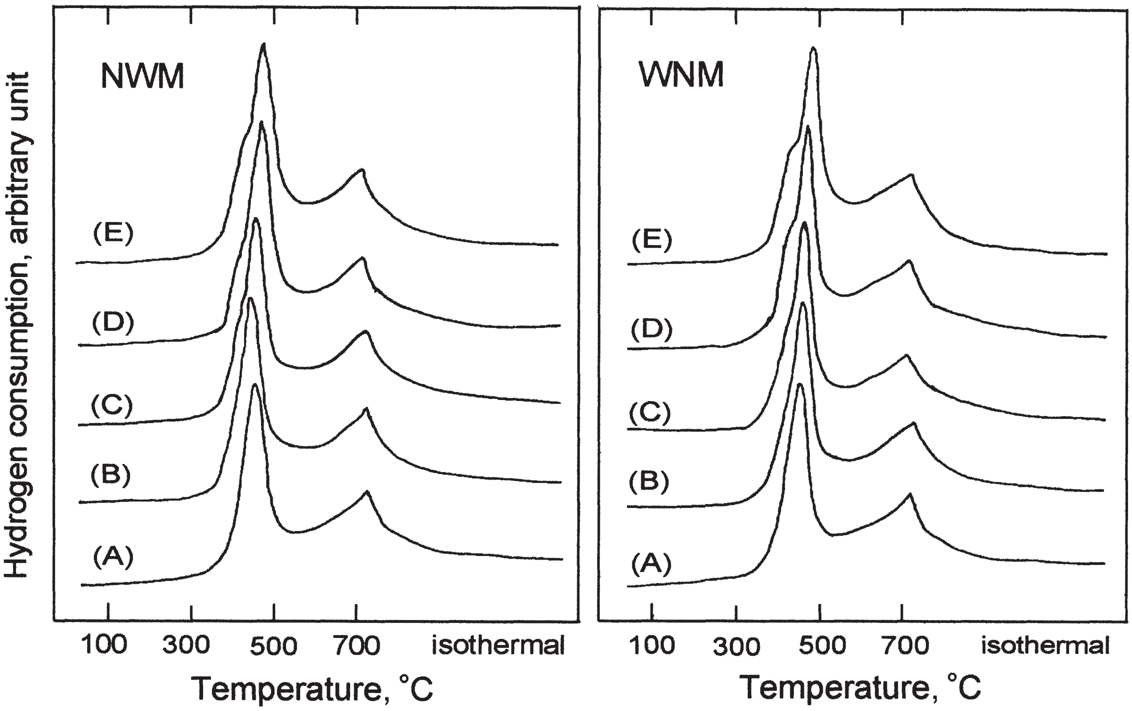

Figure 5. TPR profiles of Ni(2.14)Mo(4)/KHA (A) and the oxidic NWM and WNM series catalysts with the W/(W + Mo) atomic ratios as follows: (B) 0.025, (C) 0.05, (D) 0.1, and (E) 0.2.

smaller patches during sulfiding by virtue of the non-sulfided monomeric $WO_3$ species placed on the sparsely spaced octahedral $Mo_o$ patches. As long as the intrinsic active phase structure of the catalyst is not altered, such an increase in the planar dispersion of active phases over the support leads to the formation of the increased number of active sites and, consequently, to promoted activity.

As shown in figure 2, the activity promotion for the NiMo-based catalyst system by W incorporation is deeply dependent on the impregnation order of tungsten. The catalysts prepared by impregnating Ni onto the WMo/$\gamma$-$Al_2O_3$ catalysts showed the activity promotion with the incorporation of an appropriate amount of tungsten, but those by impregnating W onto a NiMo/$\gamma$-$Al_2O_3$ catalyst did no promotion with any content of tungsten. However, the Co-promoted Mo/$\gamma$-$Al_2O_3$ catalyst in the previous works [7,8] showed the promoted catalytic activity with W incorporation regardless of the impregnation order of tungsten, although the catalysts (WCM series) prepared by impregnating tungsten onto the CoMo/$\gamma$-$Al_2O_3$ showed somewhat higher activities than did the catalysts (CWM series) prepared by impregnating tungsten onto Mo/$\gamma$-$Al_2O_3$ followed by impregnation of cobalt.

It is, therefore, stated that the promotional effect by tungsten incorporation on the catalytic activity of alumina-supported Mo-based catalysts appear differently from the kind of catalytic promoters (Ni or Co). This may be attributed to the difference in the structure of active phases between NiMo and CoMo catalysts supported on alumina. Kemp et al. [20] reported that unpromoted and Co-promoted Mo/$\gamma$-$Al_2O_3$ catalysts have mainly the monolayered structure of active phases, $MoS_2$ and Co–Mo–S, respectively, while Ni-promoted Mo/$\gamma$-$Al_2O_3$ catalyst consists primarily of multilayered Ni–Mo–S active phase. And, it is presumed that the structure of a calcined catalyst in oxidic state is basically similar to that of the active phase in sulfide state if the oxide catalyst is sulfided in a mild condition [21].

The catalyst series WM in this study and the CoMo-based, W-incorporated catalysts (WCM and CWM) in the previous works [7,8] showed the same catalytic activity behavior with increasing content of tungsten, all exhibiting the maximal activity promotion at the W/(W + Mo) atomic ratio 0.025. Because both Mo/$\gamma$-$Al_2O_3$ and CoMo/$\gamma$-$Al_2O_3$ catalysts have primarily the monolayered structures, the presence of an appropriate amount of monomeric $WO_3$ in these catalysts makes it possible to increase the planar dispersion without significant changes in the original structure of active phases, supplying promoted catalytic activities to the catalysts.

Contrary to these Mo and CoMo catalysts, the effects of tungsten incorporation to the Ni-promoted Mo catalysts are significantly dependent on the impregnation order of tungsten and nickel to the Mo/$\gamma$-$Al_2O_3$. Particularly, the incorporation of even a small amount of tungsten into the NiMo/$\gamma$-$Al_2O_3$ results in the considerable loss of catalytic activities. It is thought that only a small content of $WO_3$ impregnated additionally onto the NiMo/$\gamma$-$Al_2O_3$ may break the multilayered Ni–Mo–O phases formed previously, resulting in a diminished catalytic activity. The sulfidation-resistant $WO_3$ species can play an effective role in increasing the planar dispersion of Mo phases, however, due to this effect, the previously formed multilayered Ni–Mo–O phases may be collapsed and prevented from being transformed into the highly active Ni–Mo–S phases during sulfidation.

However, in the case of the catalyst series of NWM, the presence of an appropriate amount of monomeric $WO_3$ species makes a high activity promotion, as observed in the catalyst Ni(2.14)W(0.1)Mo(4)/KHA of figure 2. Simultaneously, this catalyst exhibits a large oxygen uptake (figure 3) and a considerable reduction peak shift towards lower temperature (figure 5), as compared with those of Ni(2.14)Mo(4)/KHA. It is thought that most of the finally impregnated Ni species onto the W(0.1)Mo(4)/KHA catalyst may become associated with the $Mo_o$ species, forming Ni–Mo–O phases, due to much higher surface density of $Mo_o$ than the monomeric $WO_3$. This results in the formation of a larger number of the active Ni–Mo–O phases on the catalyst than on the Ni(2.14)Mo(4)/KHA catalyst. Accordingly, the oxygen uptake and the catalytic activities of the Ni(2.14)W(0.1)Mo(4)/KHA catalyst appear greater than those of Ni(2.14)Mo(4)/KHA.

Regardless of the kind of promoter used or the impregnation order of tungsten, the incorporation of tungsten in a large amount into the alumina-supported Mo-based catalysts results in lower catalytic activities. As observed from figure 4, the incorporation of higher quantity of tungsten decreases the amounts of easy-reducible $Mo_o$ species in Mo/$\gamma$-$Al_2O_3$ catalyst, resultantly making the catalyst less active. The appearance of the new reduction peak at temperature around 574 °C in the catalysts W(0.44)Mo(4)/KHA and W(1.0)Mo(4)/KHA may be attributed to the formation of W–Mo mixed oxide [22], possibly originated from the increase in the W oxide coverage on the surface of $Mo_o$ species. W–Mo mixed oxides formed at the sacrifice of the reducible $Mo_o$ species is thought not to induce any favorable effects on HDS or HYD catalytic activity.

## 5. Conclusion

As the incorporation content of tungsten increased, the HDS and HYD activities of the WMo/$\gamma$-$Al_2O_3$ catalysts (WM series) initially promoted and subsequently decreased as compared with those of their base Mo/$\gamma$-$Al_2O_3$, reaching the maximal promotion at the $W/(W+Mo)$ atomic ratio 0.025. The previous works [7,8] on the W incorporation into the Co-promoted Mo/$\gamma$-$Al_2O_3$ catalyst reported the same activity promotion as observed in this WM series irrespective of the impregnation order of tungsten. However, for the Ni-promoted Mo/$\gamma$-$Al_2O_3$ catalysts, the activity promotion behavior by W incorporation was greatly dependent on the impregnation order of tungsten. The catalysts prepared by impregnating Ni onto the WMo/$\gamma$-$Al_2O_3$ catalysts showed the same activity promotion as the WM series did, while all those by impregnating W onto a NiMo/$\gamma$-$Al_2O_3$ catalyst resulted in deactivation rather than promotion. The results ascertained that the incorporation of an appropriate amount of tungsten was basically effective in inducing catalytic activity promotion for both unpromoted Mo/$\gamma$-$Al_2O_3$ and Co-promoted Mo/$\gamma$-$Al_2O_3$ catalysts which have primarily the monolayered structure of active phases, but not for the NiMo/$\gamma$-$Al_2O_3$ catalyst which consists primarily of multilayered active phase.

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