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W-Incorporated CoMo/γ-Al_2O_3 Hydrodesulfurization Catalyst

I. Catalytic Activities

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The promotional effect of tungsten in the CoMo/γ-Al_2O_3 catalyst was studied for series of W-incorporated CoMo/γ-Al_2O_3 catalysts with different content of tungsten. Two series of the catalysts were prepared by changing the impregnation order of cobalt and tungsten onto a base Mo/γ-Al_2O_3 catalyst. Impregnation of tungsten was achieved under the condition that the pH of an aqueous impregnating solution of W anion was controlled to 9.5. The hydrodesulfurization (HDS) and hydrogenation (HYD) activities of the sulfided catalysts were evaluated by thiophene HDS and ethylene HYD reactions at atmospheric pressure, respectively. Low-temperature O_2 chemisorption at 195 K was conducted for the sulfided catalysts in order to determine the W-incorporation effects on the surface concentration of coordinatively unsaturated sites related to the catalytic activities. The dependence of catalytic activities on tungsten content showed initially an increase and subsequent decrease with increasing tungsten content. The maximum promotion of HDS and HYD activities occurred at a low content of tungsten corresponding to 0.025 in W/(W + Mo) atomic ratio regardless of the impregnation order of tungsten and cobalt. Oxygen uptake correlated well with catalytic activities. In general, the catalysts prepared by impregnating tungsten onto the CoMo/γ-Al_2O_3 showed higher activities than the catalysts prepared by impregnating tungsten onto Mo/γ-Al_2O_3 prior to impregnation of cobalt.

INTRODUCTION

Alumina-supported Co(Ni)–Mo(W) sulfide pairs are the most widely employed catalysts in petroleum oil hydrotreating processes. However, there have been various attempts to improve the performance of the conventional catalysts by applying novel preparation methods, replacing the conventional promoters with other metals, adding a third element to the catalysts, or adopting a new support material instead of γ-Al_2O_3. A number of studies on the use of some transition metals like Ti (1–3), Ni (4–7), Ru (8–10), Zn (1, 2, 11, 12), and Fe (1, 13–15) as promoters or additives to Al_2O_3-supported Mo or CoMo catalysts have been carried out in an attempt to develop new catalytic systems with improved hydrotreating performance. Recently, we reported (16) that the introduction of a small amount of tungsten into a commercial catalyst CoMo/γ-Al_2O_3 (Amocat 1A) brought about beneficial effects on the catalyst performance for hydrodesulfurization (HDS), asphaltene conversion, and conversion of heavier to lighter oil fractions during the high pressure hydrotreatment of an atmospheric residual oil feed. The initial deactivation rate of the W-added CoMo/γ-Al_2O_3 catalyst was also improved compared with that of the commercial CoMo/γ-Al_2O_3 catalyst. The tungsten added to the CoMo/γ-Al_2O_3 was expected to play a certain role in promoting the catalytic activities of the catalyst.

In this paper, we report the effects of the amount of W incorporation and the impregnation order of tungsten on the catalytic activities of the trimetallic catalysts and suggest an optimum W content. As probe reactions, thiophene HDS and ethylene hydrogenation (HYD) were conducted at atmospheric pressure to determine HDS and HYD activities of the sulfided catalysts. In addition, low-temperature O_2 chemisorption (LTOC) on the sulfided catalysts was conducted at 195 K in an attempt to quantitatively titrate active sites. The changes in the HDS and HYD activities of the catalysts are discussed in relation with the O_2 uptake.

EXPERIMENTAL

Preparation of Catalysts

Six base γ-Al_2O_3-supported catalysts of compositions Mo(4.0), Co(1.71)Mo(4.0), Co(2.14)Mo(4.87), Co(2.14)-Mo(4.0), W(5.0), and Co(2.14)W(5.0) were first prepared by incipient wetness impregnation of γ-Al_2O_3 with solutions of ammonium heptamolybdate tetrahydrate (Fluka,

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TABLE 1

List of Prepared Catalysts

	Atomic ratio of metals			Wt% of metal oxides			BET area
Notation	$\frac{W}{W+Mo}$	$\frac{Co}{Co+Mo}$	$\frac{Co}{Co+W+Mo}$	CoO	WO_3	MoO_3	(m^2/g)
Basis catalysts							
Mo(4.0)[a]				—	—	13.3	—
Co(1.71)Mo(4.0)		0.3		2.9	—	12.9	135
W(5.0)				—	24.0	—	—
Co(2.14)W(5.0)			0.3	3.2	—	23.0	132
CWM series based on Mo(4.0)							
Co(1.71)W(0.05)Mo(4.0)	0.0125	0.3	0.3	2.9	0.22	12.9	133
Co(1.71)W(0.10)Mo(4.0)	0.025	0.3	0.29	2.9	0.48	12.8	131
Co(1.71)W(0.21)Mo(4.0)	0.05	0.3	0.29	2.9	1.11	12.8	131
Co(1.71)W(0.44)Mo(4.0)	0.1	0.3	0.28	2.8	2.35	12.5	130
Co(1.71)W(1.0)Mo(4.0)	0.2	0.3	0.25	2.7	4.81	12.3	129
WCM series based on Co(1.71)Mo(4.0)							
W(0.05)Co(1.71)Mo(4.0)	0.0125	0.3	0.3	2.9	0.23	12.9	134
W(0.1)Co(1.71)Mo(4.0)	0.025	0.3	0.29	2.9	0.51	12.8	132
W(0.21)Co(1.71)Mo(4.0)	0.05	0.3	0.29	2.9	1.04	12.8	131
W(0.44)Co(1.71)Mo(4.0)	0.1	0.3	0.28	2.8	2.31	12.5	133
W(1.0)Co(1.71)Mo(4.0)	0.2	0.3	0.25	2.7	4.83	12.3	132
WCM-A catalysts with their own CoMo bases different each other							
Co(2.14)Mo(4.87)	—	0.3	—	3.5	—	15.3	120
W(0.12)Co(2.14)Mo(4.87)	0.025	0.3	0.3	3.5	0.61	15.1	123
Co(2.14)Mo(4.0)	—	0.35	—	3.6	—	12.8	138
W(1.0)Co(2.14)Mo(4.0)	0.2	0.35	0.3	3.4	4.89	12.2	130

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

$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, 99 + %), ammonium metatungstate (Fluka, $(NH_4)_6H_2W_{12}O_{40}$, 97 + %), and cobalt nitrate hexahydrate (Junsei, $Co(NO_3)_2 \cdot 6H_2O$, GR grade) as required. The numbers in parentheses followed by each catalytic component indicate the number of atoms per square nm of support surface area. The γ-Al_2O_3 used as a support is 60–100 mesh-sized Nishio KHS alumina whose physical properties are as follows: surface area, 160 m^2/g; pore volume, 0.67 cm^3/g; and mean pore diameter, 167 Å. To prepare CoMo or CoW catalysts, molybdenum or tungsten was first impregnated onto the alumina support and then cobalt was impregnated. 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.

Two series of γ-Al_2O_3-supported trimetallic catalysts with different contents of tungsten were prepared varying the order of tungsten impregnation. Series of catalysts denoted as CWM were prepared by impregnating tungsten onto the base catalyst Mo(4.0) before impregnation of cobalt. The other series of catalyst denoted as WCM were obtained by impregnation of tungsten onto Co(1.71)Mo(4.0). In order to vary the atomic ratio of W/(W + Mo) from 0.0125 to 0.2, the tungsten content of the impregnation solutions was simply increased with respect to the fixed amount of Mo or CoMo. Afterward, the term W/(W + Mo) will always refer to atomic ratio of metals. In order to observe the catalytic effects solely originating from the composition differences excluding any contributions due to the difference in total metal loading, two additional WCM catalysts which are equivalent to each other in total metal content but different in W/(W + Mo) atomic ratio were prepared. These additional WCM catalysts, denoted as WCM-A, of compositions W(0.12)Co(2.14)Mo(4.87) and W(1.0)Co(2.14)Mo(4.0) are nearly equal in total metal loadings but different in W/(W + Mo) atomic ratio, 0.025 and 0.2, respectively. 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 cobalt nitrate or ammonium molybdate was not adjusted. The pH control of W solution was based on reports that the monomeric species of tungsten anion WO_4^{2-} predominated in alkaline solution of pH around 9.5 (17, 18) and that a more flat impregnation profile of tungsten across the alumina support was achieved from high pH solutions (19).

Physical properties and metal atomic ratios of the prepared catalysts are listed in Table 1. X-ray fluorescence (Aroma EX-6500) was used to determine the bulk concentration of tungsten, cobalt, and molybdenum. BET surface areas of the catalyst samples were determined by nitrogen adsorption using a Quantachrome Autosorb-I. All the prepared catalysts were further crushed to the particles of 100–300 mesh size before the use in experiments.

Measurements 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. In both reactions, 100 mg of catalyst samples were first heated to 450°C in purified N_2 for 0.5 h (Hanguk UHP grade) and sulfided *in situ* in a gas mixture of 10% H_2S (Matheson CP grade) and 90% H_2 (Hanguk UHP grade) at 450°C for 2 h. The sulfided catalysts were flushed with N_2 for 0.5 h at the sulfiding temperature and then cooled to the desired reaction temperature. Then the N_2 flow was replaced with a stream of H_2 containing the reactant. In case of HDS, liquid thiophene (Aldrich, $99+\%$) was introduced into the reaction system at a rate of 0.31 cm^3/h (1.075 μmol/s) using a syringe pump and mixed with hydrogen flow at a rate of 30 cm^3/min (22.322 μmol/s) in an evaporator. For HYD, ethylene (Matheson, 99.5% min) was fed into a H_2 stream of 30 cm^3/min (22.322 μmol/s) at a rate of 5 cm^3/min (3.72 μmol/s). All the gases except H_2S were further purified with oxytraps (HP Oxygen Scavenger) and molecular sieve traps. Both reactions reached steady state conditions after 2 h of the start of run. Reaction products were analyzed by GC (HP 5890 II) employing a Porapak Q column and a thermal conductivity detector.

The HDS and HYD reaction rate constants were calculated by assuming that thiophene or ethylene conversion proceeded according to the first order plug flow kinetics, i.e, $k_{\mathrm{HDS\ or\ HYD}} = F/(\mathrm{g\ cat}) \cdot \ln\,(1 - X/100)$, where k_{HYD} or k_{HYD} is the rate constant, μmol of thiophene or ethylene converted per second per gram of catalyst, F is μmol feed rate of thiophene or ethylene per second, and X is percentage conversion of thiophene or ethylene. Every conversion value used to calculate the reaction rate constant was a mean of three successive measurements although there was a good reproducibility within 1% variations among the successive conversions.

Low-Temperature Oxygen Chemisorption by Dynamic Pulses

Oxygen chemisorption on the sulfided catalyst samples was measured at 195 K using the same reactor employed for HDS and HYD reactions. The sample size in each LTOC experiment was 400 mg of oxide catalyst and was kept constant for all runs. The oxide catalyst samples were routinely pretreated and sulfided *in situ* in the same manner as used for HDS or HYD reaction experiments. He was used instead of N_2. The freshly sulfided samples were purged with purified He for 15 min at the sulfiding temperature and then cooled to room temperature within 30 min in He flow (30 cm^3/min). Subsequently, the reactor was immersed into a cold bath of acetone and finely crushed dry ice. About 15 min after immersion of the reactor into the cold bath, the first pulse of O_2 (0.05 cm^3 STP) was injected into the He carrier gas flow (30 cm^3/min) by means of a six port valve with a sample loop size of 0.05 cm^3. Successive injections were made at 5 min intervals until three consecutive effluent O_2 peaks of equal area were obtained using GC (HP 5890 II) equipped with a thermal conductivity detector.

RESULTS

HDS and HYD Activities

The relative changes in the thiophene HDS and ethylene HYD reaction rate constants of both CWM and WCM series catalysts with increasing content of tungsten are shown in Figs. 1 and 2. The relative changes in k_{HDS} or k_{HYD} mean the percentage changes of the reaction rate constants of both series of catalysts as compared with the value of k_{HDS} or k_{HYD} of the base catalyst Co(1.71)Mo(4.0), which is shown in Table 2. The HDS and HYD reaction rate constants of Co(2.14)W(5.0) and the WCM-A catalysts and their base CoMo catalysts are also presented in Table 2.

As shown in Figs. 1 and 2, HDS and HYD activities of both CWM and WCM series catalysts increase sharply with lower loadings of tungsten but decrease with further increase in tungsten content. The maximum increases

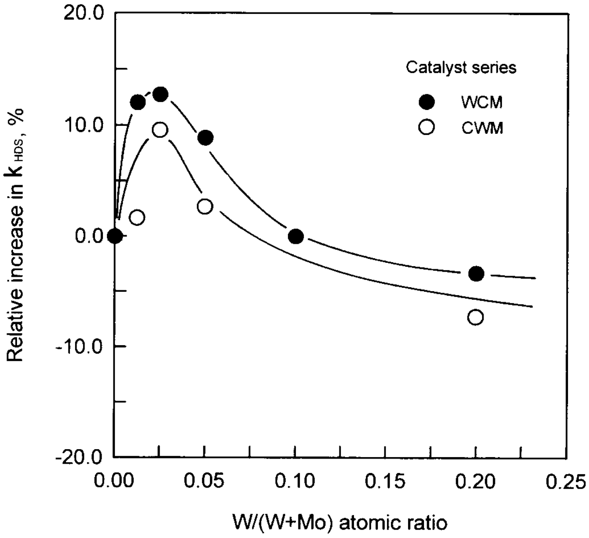

FIG. 1. Percentage changes in the thiophene HDS rate constants at 350°C of both CWM and WCM series catalysts of various tungsten contents relative to the k_{HDS} of Co(1.71)Mo(4.0).

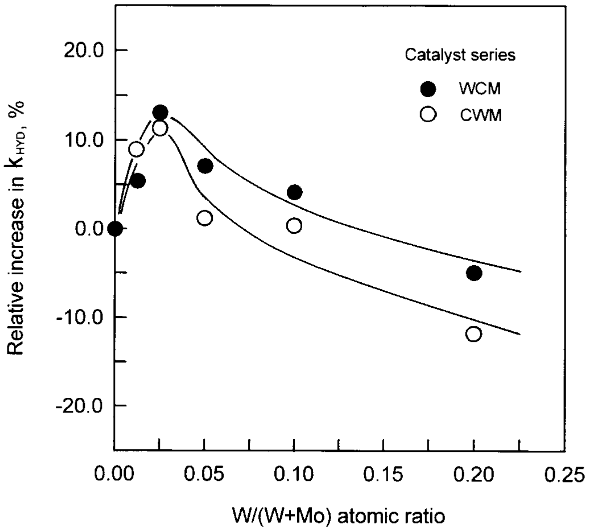

FIG. 2. Percentage changes in the ethylene HYD rate constants at 275°C of both CWM and WCM series catalysts of various tungsten contents relative to the k_{HYD} of Co(1.71)Mo(4.0).

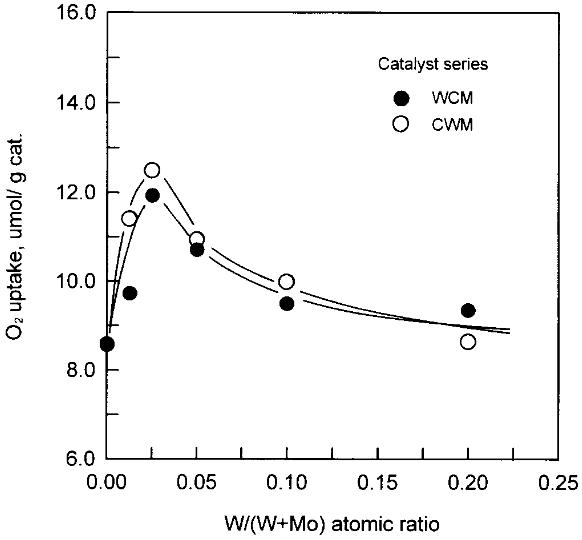

FIG. 3. Oxygen uptake of the sulfided CWM and WCM series catalysts of various tungsten contents as compared with that of Co(1.71)Mo(4.0).

in the HDS and HYD activities are observed at 0.025 W/(W + Mo). It is observed that the increases in both HDS and HYD activities are higher for the WCM catalysts than for the CWM catalysts. When considering the HDS and HYD activities of WCM-A catalysts and their bases, as presented in Table 2, it can be found that the activities of W(0.12)Co(2.14)Mo(4.87) increase but those of W(1.0)Co(2.14)Mo(4.0) decrease as compared with their respective CoMo bases. The incorporation content of tungsten in the former and the latter correspond to 0.025 and 0.2 in W/(W + Mo) atomic ratio, respectively. Both of WCM-A catalysts are nearly the same in their total metal loadings but are different in the composition of tungsten and molybdenum. Co(2.14)W(5.0) shows much lower activities than Co(1.71)Mo(4.0).

TABLE 2

HDS and HYD Reaction Rate Constants of Some Base Catalysts

Catalysts	k_{HDS} at 350°C μmol thiophene (s · g cat)	k_{HYD} at 275°C μmol ethylene (s · g cat)
Base catalysts		
Co(1.71)Mo(4.0)	5.2	12.6
Co(2.14)W(5.0)	1.4	4.0
WCM-A catalysts and their CoMo bases		
Co(2.14)Mo(4.87)	4.8	11.3
W(0.12)Co(2.14)Mo(4.87)	5.8	12.5
Co(2.14)Mo(4.0)	5.5	13.1
W(1.0)Co(2.14)Mo(4.0)	4.6	12.1

Oxygen Uptake

The oxygen uptake of the sulfided catalysts of both CWM and WCM series catalysts was plotted as a function of tungsten content as shown in Fig. 3. Oxygen uptake is higher for the catalysts of the CWM series than the WCM series. When comparing Fig. 3 with Figs. 1 and 2, it can be observed that the trends of both oxygen uptake and activity behavior are quite similar, indicating that a correlation exists between the catalytic activity and the oxygen uptake. Similar results were obtained for the WCM-A catalysts although they are not presented here.

DISCUSSION

Figures 4 and 5 show Arrhenius plots on thiophene HDS for some typical CWM and WCM series catalysts as well as Co(1.71)Mo(4.0), and for the WCM-A catalysts with their respective CoMo base in comparison with Co(2.14)W(5.0), respectively. As far as molybdenum-based catalysts are concerned, the thiophene HDS activation energies of the catalysts are nearly the same regardless of the incorporation of tungsten within the present experimental range. It is apparent that the catalysts of the tungsten composition corresponding to 0.025 W/(W + Mo) have higher frequency factors than the CoMo base catalysts, but the catalysts containing higher content of tungsten result in lower frequency factors as compared with the CoMo base catalysts. Co(2.14)W(5.0) has HDS activation energy higher than the molybdenum-based catalysts, suggesting

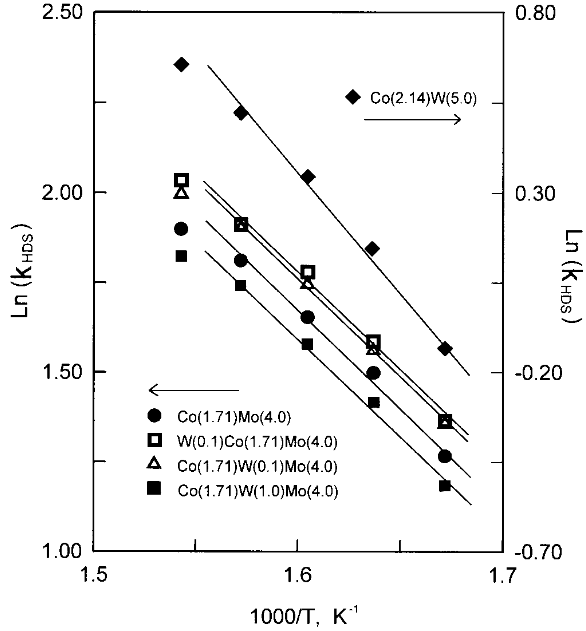

FIG. 4. Arrhenius plot for thiophene HDS reaction over the catalysts of Co(1.71)Mo(4.0) and some typical CWM and WCM series in comparison with Co(2.14)W(5.0) catalyst.

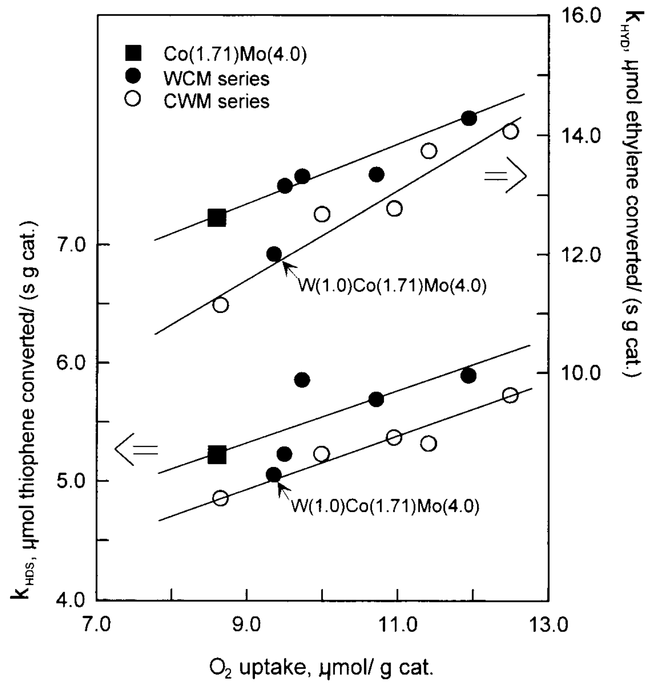

FIG. 6. Correlation of the reaction rate constants for thiophene HDS at 350°C and ethylene HYD at 275°C with oxygen uptake in the CWM and WCM series catalysts.

that intrinsic activity for HDS of CoW catalyst is lower than that of CoMo catalyst. These results show that the HDS and HYD activities of the W-incorporated catalysts increased or decreased depending on their tungsten composition. This indicates that a small amount of incorporated tungsten plays a role of promoter. The enhancement in catalytic activities by the tungsten incorporation is projected by the increase in the frequency factor without significant changes in the activation energy, strongly suggesting that the promotion by tungsten incorporation results mainly from an increase in the number of active sites rather than a change in the nature of active sites.

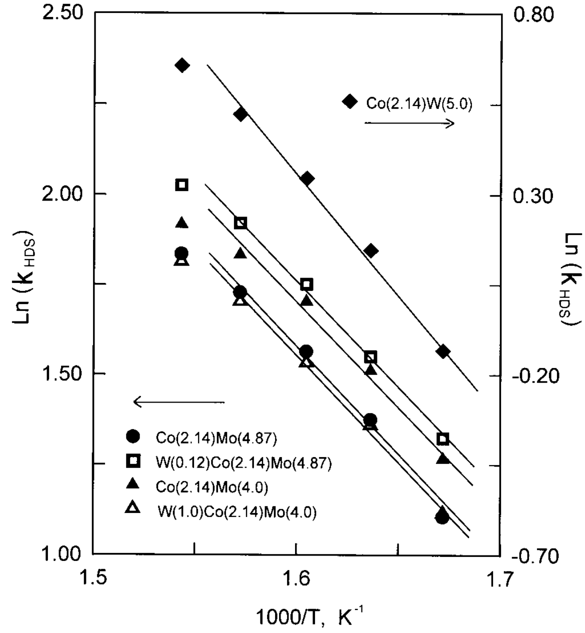

FIG. 5. Arrhenius plot for thiophene HDS reaction over the WCM-A and their CoMo base catalysts in comparison with Co(2.14)W(5.0) catalyst.

For the alumina-supported Mo- or W-based catalysts, coordinatively unsaturated sites (CUS) 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 (20–26). In order to measure the surface concentration of CUS and its correlation with catalytic activity, LTOC has been employed in a number of works (20–22). It is also believed that for sulfided catalysts, oxygen chemisorbs selectively (24, 26) and dissociatively (25, 26) on these CUS at temperatures around 195 K without attacking the bulk of the sulfide phase. Figure 3 suggests that an adequate amount of tungsten in CoMo catalysts plays a role in facilitating the creation of CUS on the catalyst, but the excess amount of tungsten results in decreasing CUS sites.

The HDS and HYD activities of both CWM and WCM series catalysts versus the oxygen uptake are presented in Fig. 6. For each catalyst series, the catalytic activity and the oxygen uptake are observed to be linearly correlated. It is found from Fig. 6 that WCM series catalysts result in higher activities in both HDS and HYD than CWM series catalysts at the same oxygen uptake level and that HYD activity is more dependent on the oxygen uptake than is HDS activity. As shown in Figs. 4 and 5 and Table 2, the intrinsic HDS and HYD activities of CoMo catalysts are higher than those of CoW catalysts. According to the "Co–Mo–S" model proposed by Topsoe *et al.* (27–29), the active metal sulfide phases in the two catalysts of CoMo/γ-Al_2O_3 and CoW/γ-Al_2O_3 would be Co–Mo–S and Co–W–S, respectively. The previous reports (30, 31) that the thiophene HDS and toluene HYD activities of CoMo/γ-Al_2O_3 were higher than those of CoW/γ-Al_2O_3 are in agreement with our results.

The existence of two different correlation lines in Fig. 6 might be attributed to the relative contributions of more active Co–Mo–S and less active Co–W–S phase to the catalytic activity. The activities of WCM series catalysts are thought to be contributed mainly by the Co–Mo–S phase because they are prepared by impregnating tungsten onto the CoMo/Al_2O_3 in which Co and Mo have been chemically associated with each other before W impregnation. On the other hand, activities of CWM series catalysts are attributed not only to Co–Mo–S but to Co–W–S in a relatively larger proportion than WCM catalysts because they are prepared by impregnating tungsten onto Mo/Al_2O_3 followed by cobalt, resulting in the increased probability of forming Co–W–O instead of Co–Mo–O phases. Although the catalyst W(1.0)Co(1.71)Mo(4.0) belongs to the WCM series, the correlation between the catalytic activities and the oxygen uptake in this catalyst is found to be represented by the line corresponding to the CWM series rather than the WCM series as observed in Fig. 6. This indicates that even though this catalyst was prepared by the WCM procedure, a large portion of more active Co–Mo–O structures of the base CoMo/γ-Al_2O_3 could be converted to less active Co–W–O structures if the content of tungsten added to the base catalyst was high in the case of W(1.0)Co(1.71)Mo(4.0). Hence, the catalyst becomes less active due to its lower average intrinsic activity although it has more catalytic sites than the base catalyst, Co(1.71)Mo(4.0). When comparing the reaction rate constants between HDS and HYD, it can be understood that the reaction of ethylene HYD is more facile than that of thiophene HDS. Consequently, the reaction rate of HYD can be more enhanced by the increase in the total number of active sites regardless of the active phase species, Co–Mo–S or Co–W–S, at least as far as they have some extent of HYD activity.

In order to consider the catalytic behavior of the W-added CoMo/γ-Al_2O_3 catalysts in the heavy oil hydrotreatment under high H_2 pressure, the relative initial reaction conversions over another series of WCM catalysts are shown in Fig. 7. Data presented in Fig. 7 originated from our previous publication (16) where further experimental details could be found. The W-added catalysts used in those high pressure hydrotreatment experiments were prepared by impregnating tungsten onto a commercial CoMo/γ-Al_2O_3 catalyst named Amocat 1A (CoO: 2.5 wt%; MoO_3: 9.8 wt%). The conversion of heavier to lighter oil fractions was defined as how much the oil fractions of $C_{21}+$ hydrocarbons were converted to lower carbon number hydrocarbon fractions. Although the catalysts were prepared from a commercial CoMo/γ-Al_2O_3 and the reaction was performed under high H_2 pressure (6.9 MPa) and temperature (420°C), it can be observed in Fig. 7 that the effects of W incorporation on the conversions are nearly identical with those on the atmospheric probe reactions as shown in Figs. 1 and 2. The maximum conversions in the high pressure reaction were achieved over the catalyst with WO_3 content of 0.5 wt% which corresponds to 0.026 W/(W + Mo). It is worthwhile to note that the optimum W contents in all the WCoMo/γ-Al_2O_3 catalyst series including the WCM series catalysts based on Amocat 1A approach to a single composition corresponding to 0.025 W/(W + Mo).

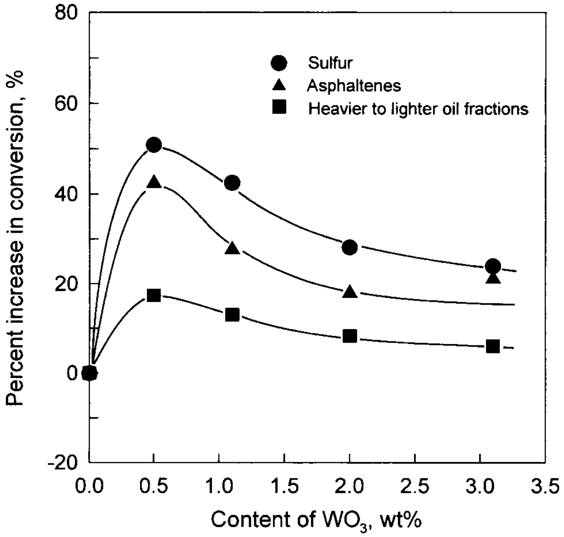

FIG. 7. Effects of the tungsten content added to Amocat 1A CoMo/γ-Al_2O_3 catalyst on the high pressure hydrotreating reaction conversions of atmospheric residual oil. Data taken from the reference (16).

The increase in the asphaltene conversion as shown in Fig. 7 might be due to the increase in the number of active sites having some HYD activity in agreement with the previous report (31) that the conversion of asphaltenes is more facilitated over the catalyst of more hydrogenative and less acidic character. The dispersion or the number of active sites can be considered to be more important than the migintude of intrinsic activity of the active site when the catalyst is employed to hydrotreat a heavy residual oil feed containing a large amount of organometallic compounds and asphaltenes which are the main causes of catalyst deactivation. Eijbouts *et al.* (33) found that high-activity commercial catalysts have very high dispersion of active metal sulfide phases. It is generally accepted that the initial deactivation of the supported catalyst is related to coke deposition (34–36). Diez *et al.* (34) proposed that the active metal sulfide phase is maintained relatively coke free as a result of a self-cleaning process but activity is lost as coke accumulates on the Al_2O_3 support, growing in thickness and resulting in edge blockage of the active metal sulfide phase. Eijbouts *et al.* (37) suggested that the deactivation is due to the loss of the active phase dispersion during hydrotreating reaction. The catalytic performance and the service life of the catalyst are directly related to the dispersion of active phase. It was previously reported by us (16) that the initial deactivation rates of the W-added CoMo/γ-Al_2O_3 catalysts were decreased with the increase in tungsten content as well as the beneficial effects on the reaction performance as shown in Fig. 7. These effects of W incorporation may be attributed mainly to the increase in the number of active sites as it can be seen from Fig. 6 that oxygen uptakes of all the catalysts of the WCM series are higher than their base catalyst, Co(1.71)Mo(4.0).

CONCLUSION

HDS and HYD activities of the W-incorporated CoMo/γ-Al_2O_3 catalysts were promoted or suppressed depending on the amount of tungsten. The promotional effect was observed for the catalysts containing a relatively low content of tungsten whereas the catalysts containing a higher content of tungsten showed an inhibition effect. The maximum activity promotion occurred at a low content of tungsten corresponding to 0.025 in W/(W + Mo) atomic ratio regardless of the impregnation order of tungsten and the composition of CoMo/γ-Al_2O_3 base catalyst. The changes in the rate constants of HDS and HYD reactions with tungsten content correlated well with the oxygen uptake of the sulfided catalysts at 195 K. The catalysts (WCM) prepared by impregnating tungsten onto the CoMo/γ-Al_2O_3 resulted in higher activities than did the catalysts (CWM) prepared by impregnating tungsten onto Mo/γ-Al_2O_3 followed by impregnation of cobalt.

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