CHARACTERIZATION OF HYDRODESULFURIZATION CATALYST PREPARED BY IMPREGNATING COBALT NITRATE SOLUTION ONTO THE SULFIDED MoO_3/Al_2O_3 CATALYST

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Abstract — $CoMo/Al_2O_3$ catalysts were prepared by impregnating Cobalt nitrate solution into oxidic or sulfided Mo/Al_2O_3. The properties of $CoMo/Al_2O_3$ catalysts were characterized by XRD, TPS, oxygen chemisorption and ESR. Catalytic activity of $CoMo/Al_2O_3$ catalyst was evaluated by thiophene HDS as a probe reaction. When $CoMo/Al_2O_3$ catalyst was prepared by impregnating Cobalt nitrate solution into sulfided Mo/Al_2O_3, the interaction between Mo and alumina became weaker and the formation of synergic phase was facilitated. These structural changes may explain higher HDS activity of $CoMo/Al_2O_3$ catalyst prepared by impregnating Cobalt nitrate solution into sulfided Mo/Al_2O_3.

Key words: Hydrodesulfurization, $CoMo/Al_2O_3$, TPS, XRD, ESR

INTRODUCTION

$CoMo/Al_2O_3$ catalyst has been widely used as a hydrodesulfurization (HDS) catalyst for many years. The structure and HDS activity of $CoMo/Al_2O_3$ catalyst were influenced by many parameters such as the impregnation order of Co and Mo [Chung and Massoth, 1980a, b] impregnation method [Caceres et al., 1984, 1985], sulfidation temperature [Kim and Woo, 1991a] and additive effects [Kim and Woo, 1991b, 1992]. Recently the catalytic activities of $CoMo/Al_2O_3$ catalysts prepared by impregnating Co into sulfided Mo catalysts were briefly reported [de Beer et al., 1974, 1976b; Duchet et al., 1983]. Co-promoted catalyst prepared by impregnating Co into sulfided Mo catalyst showed a higher HDS activity than Co-promoted catalyst prepared by impregnating Co to oxidic Mo catalyst, regardless of the kind of support. However, the reason for higher HDS activity is ambiguous yet. In present study the effect of the sulfidation treatment in the preparation procedure on the physicochemical properties of $CoMo/Al_2O_3$ catalyst was investigated. The properties of $CoMo/Al_2O_3$ were characterized by XRD, TPS, oxygen chemisorption and ESR. Catalytic activity in the HDS reaction was evaluated with thiophene HDS reaction.

EXPERIMENTAL

1. Catalyst Preparation

Mo/Al_2O_3 catalyst was prepared by the incipient wetness method with an aqueous ammonium heptamolybdate solution (Strem Chem. Co.). The pore volume and the surface area of γ-alumina (Strem Chem. Co.) were 0.25 cm^3/g and 220 m^2/g, respectively. After impregnation, catalyst was dried at 373 K for 6 hr and calcined at 773 K for 6 hr. Conventional $CoMo/Al_2O_3$ catalyst (Type I) was prepared by impregnating aqueous cobalt nitrate solution into calcined Mo/Al_2O_3, followed by drying and calcining in the

same manner as in the preparation of Mo/Al_2O_3 catalyst.

$CoMo/Al_2O_3$ catalyst (Type II) was prepared as follows. Calcined Mo/Al_2O_3 sample was sulfided with a mixed flow (40 cm^3/min) of 10% H_2S (Matheson CP grade) and 90% H_2 (Matheson UHP grade) for 12 h at various temperatures. Sulfided Mo sample was flushed with N_2 at the sulfidation temperature for 2 h and cooled to room temperature in N_2. Then oxygen pulse was injected via a six-port valve until there was no consumption of oxygen, because the abrupt contact with air destroys Mo sulfide structure [de Beer et al., 1976a; Yoshimura et al., 1988]. In order to prepare $CoMo/Al_2O_3$ catalyst aqueous cobalt nitrate solution was impregnated into sulfided Mo/Al_2O_3 sample, dried at 373 K for 6 hr and calcined at 773 K for 6 hr in N_2. $CoMo/Al_2O_3$ catalysts (Type I and II) contained 9.32 wt% of Mo (3.28 Mo atoms/nm^2) and 1.59 wt% of Co (0.98 Co atoms/nm^2). $MoS(x)Co/Al_2O_3$ represents $CoMo/Al_2O_3$ catalyst (Type II) where x represents the sulfiding temperature to prepare sulfided Mo/Al_2O_3 samples.

2. XRD

X-ray diffractometer (Rigaku Co.) was equipped with a Cu X-ray tube. Tube voltage and current were 35 kV and 15 mA, respectively. The XRD spectra for $CoMo/Al_2O_3$ catalysts sulfided at various temperatures for 2 h were *ex-situ* recorded at room temperature.

3. Temperature Programmed Sulfiding (TPS)

The samples were calcined at 773 K for 2 h and cooled to room temperature with He. Calcined samples were exposed to the sulfiding gas (20 cm^3) until the signal was stabilized. The sulfiding gas was composed of 4% H_2S (Matheson CP grade), 16% H_2 (Matheson UHP grade) and 80% He. After the stabilization was reached, the samples were heated to 1073 K at a rate of 10 K/min. The effluents were analyzed by mass spectrometer (VG Quadrupoles Co., SX-300).

4. ESR

The ESR spectra were taken at room temperature with a ESR spectrometer (ER 200D-SRC, Bruker Co.) which has a single cavity and is operated in X-band microwave frequency (9.45 GHz). α,α-Diphenyl-β-picrylhydrazyl (DPPH) has been used to calibrate

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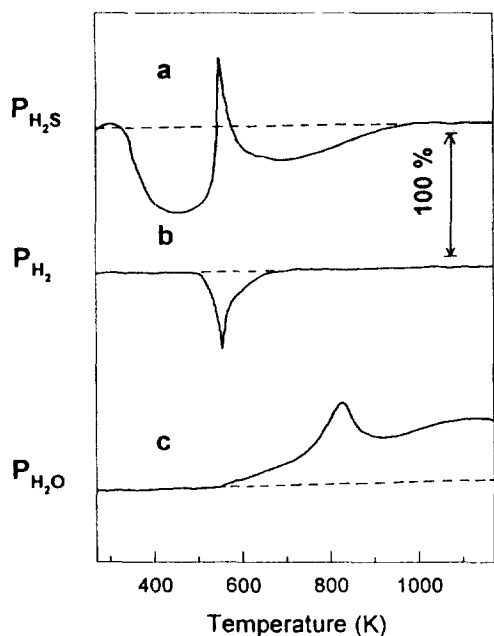
Fig. 1. Typical patterns of TPS of calcined Mo catalyst.
(a) H₂S, (b) H₂ and (c) H₂O

Fig. 2. TPS patterns (H₂S) of Mo/Al₂O₃ sample.
(a) calcined Mo/Al₂O₃, (b) Mo/Al₂O₃ sulfided at 673 K and contacted with air at room temperature, (c) Mo/Al₂O₃ sulfided at 873 K and contacted with air at room temperature, and (d) Mo/Al₂O₃ sulfided at 1073 K and contacted with air at room temperature.

g factor (the spectroscopic splitting factor). An *in-situ* ESR quartz reactor with a side-arm tube was designed to avoid air-contact. To remove physisorbed species, sulfided catalysts were evacuated at 10⁻¹ torr for 10 min at room temperature.

5. Oxygen Chemisorption

Experiment was carried out with a dynamic adsorption method in GC equipped with TCD. Sulfided catalyst was flushed for 0.5 h and cooled to 303 K in N₂. A pulse of oxygen of known volume was introduced by a six-port valve until the peak area of oxygen effluent had a constant value within 1%.

6. Thiophene Hydrodesulfurization

0.1 g of catalyst was heated to 673 K in N₂ for 0.5 h, then sulfided with a mixed flow (40 cm³/min) of 10% H₂S (Matheson CP grade) and 90% H₂ (Matheson UHP grade) for 2 h. Sulfided catalyst was flushed with N₂ for 0.5 h and then cooled to the reaction temperature of 573 K. Liquid thiophene (99%⁺, Aldrich) was introduced by a syringe pump. The flow rate of thiophene was 6.55×10^{-5} mol/min and the mole ratio of H₂/thiophene was 18. Steady state was achieved after 2 h. Reaction products were analyzed by GC (Varian Aerograph Co., model 920) equipped with OV-101 column.

RESULTS

1. TPS

The TPS spectra of Mo/Al₂O₃ are shown in Fig. 1. There are two regions of H₂S consumption: below 500 K (region I) and above 600 K (region II). H₂S production accompanied by a H₂ consumption occurred between 500 K and 600 K. H₂O production began to occur at 550 K and reached at maximum at 820 K as shown in Fig. 1(c). There were two contradictory reports that H₂O production and H₂S consumption occur simultaneously [Arnoldy et al., 1985a] and that H₂O production occurs after the signal of H₂S consumption [Stuchly et al., 1987]. The H₂O signal which remained above 950 K without a concurrent change in the H₂S
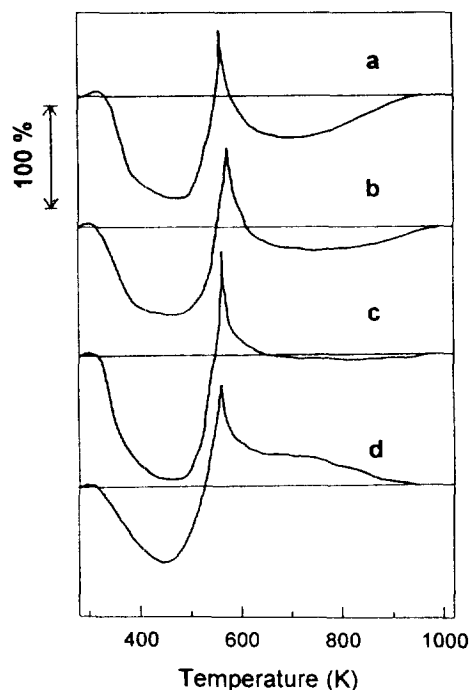
and H₂ signals, originates from the dehydration of alumina, because the sample was calcined only at 773 K before TPS. The colour of the Mo catalyst changed from yellowish-white to grayish black due to the adsorption of H₂S during stabilization at room temperature. The H₂S adsorbed on the Mo catalyst desorbed below 373 K without H₂O production. Fig. 2 showed TPS spectra of Mo/Al₂O₃ sample sulfided at various temperatures and contacted with air at room temperature. The amount of H₂S consumed in region II was much less in Mo/Al₂O₃ sample sulfided and contacted with air than in Mo/Al₂O₃ sample calcined only. And the amount of H₂S consumption decreased with increasing sulfiding temperature. And the amount of H₂S production increased in Mo/Al₂O₃ sample sulfided and air-contacted.

2. XRD

XRD patterns of CoMo/Al₂O₃ sulfided at 873 K and 1073 K are shown in Fig. 3. XRD pattern due to the crystalline Mo sulfide was not found in CoMo/Al₂O₃ catalyst (Type I) sulfided at 873 K. When sulfiding at 1073 K, XRD pattern assigned to (100) plane of the crystalline Mo sulfide ($2\theta = 33.0°$ and 33.6°) [Candia et al., 1984; Pollack et al., 1979] appeared around $2\theta = 33°$. However, when sulfiding MoS(873)Co/Al₂O₃ catalyst (Type II) at 873 K, XRD pattern arising from the crystalline Mo sulfide appeared at $2\theta = 33°$. In MoS(1073)Co/Al₂O₃ catalyst (Type II) sulfided at 1073 K, there was XRD pattern at $2\theta = 14°$ assigned to (002) plane of the crystalline Mo sulfide [Candia et al., 1984a; Pollack et al., 1979] and the intensity of XRD pattern at $2\theta = 33°$ increased.

3. ESR

There are serveral ESR bands in ESR spectra of Fig. 4. The description of ESR bands are followings. ESR band (I) at g = 1.93
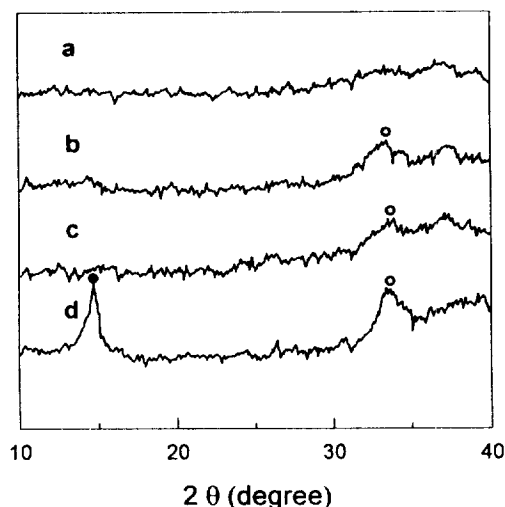
Fig. 3. XRD spectra for CoMo/Al₂O₃ catalysts sulfided at various temperatures.

(a) CoMo/Al₂O₃ (Type I) sulfided at 873 K, (b) CoMo/Al₂O₃ (Type I) sulfided at 1073 K, (c) MoS(873)Co/Al₂O₃ sulfided at 873 K, and (d) MoS(1073)Co/Al₂O₃ sulfided at 1073 K. (○) (100) plane of the crystalline molybdenum sulfide and (●) (002) plane of the crystalline molybdenum sulfide.
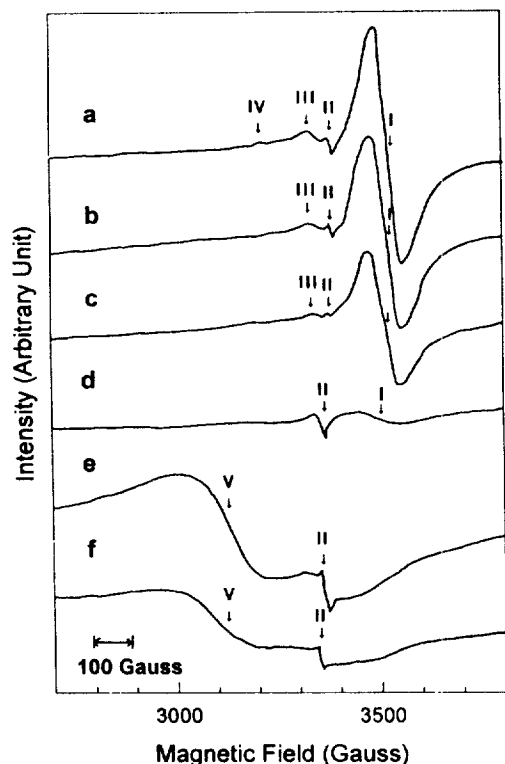

Fig. 4. ESR spectra for CoMo/Al₂O₃ catalysts (Type I) sulfided at various temperatures.

(a) 673 K, (b) 773 K, (c) 873 K, (d) 973 K, (e) 1073 K, and (f) Co/Al₂O₃ sulfided at 1073 K.

has been assigned to oxo-Mo^{+5} interacting with alumina support [Derouane et al., 1986; Bhaduri et al., 1983] while ESR band (III) at 2.05 to Mo species in sulfur environments [Derouane et
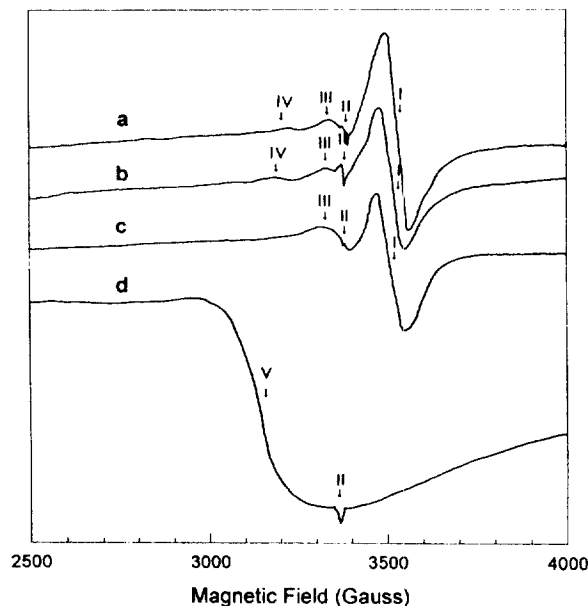

Fig. 5. ESR spectra for CoMo/Al₂O₃ catalysts (Type II) sulfided at various temperatures.

(a) CoMo/Al₂O₃ (Type I) sulfided at 673 K, (b) MoS(673)Co/Al₂O₃ sulfided at 673 K, (c) MoS(873)Co/Al₂O₃ sulfided at 873 K, and (d) MoS(1073)Co/Al₂O₃ sulfided at 1073 K.

al., 1986; Konings et al., 1981]. ESR band (II) at g=2.01 was assigned to sulfur species associated with the support [Derouane et al., 1986]. Band (IV) at g=2.12 was assigned to CoMo synergic phase such as Mo^{-3}-S-Co^{+2} [Konings et al., 1982], Mo^{+4}-S-Co^{+2} [Derouane et al., 1986] or Mo^{+5}-S-Co^{+2} [Oliver et al, 1988]. Broad band (V) at g=2.16 [Hpp(peak to peak width)=200 Gauss] was assigned to cobalt sulfide [Lo Jacono et al., 1973; Bhaduri and Mitchell, 1982; Gajardo et al., 1982].

As sulfiding temperature increased, the intensity of ESR band (I) became weaker and finally disappeared after sulfiding CoMo /Al₂O₃ catalyst (Type I) at 1073 K (Fig. 4). Also the intensity of ESR band (II) became stronger with increasing sulfiding temperature. Broad band (V) appeared when sulfided at 1073 K [Fig. 4(e)]. A similar broad band (V) was also observed after sulfiding Co/Al₂O₃ at 1073 K [Fig. 4(f)]. When sulfiding MoS(673)Co/Al₂O₃ catalyst (Type II) at 673 K, the intensity of band (II) increased while the intensity of band (I) decreased (Fig. 5). And the intensity of ESR band (IV) in MoS(673)Co/Al₂O₃ catalyst (Type II) was stronger than that in CoMo/Al₂O₃ catalyst (Type I). When sulfided at 1073 K, the intensity of ESR band (V) in MoS(1073)Co/Al₂O₃ catalyst (Type II) was stronger than that in Co/Al₂O₃ catalyst (Type I) and ESR band (I) completely disappeared in MoS(1073)-Co/Al₂O₃ catalyst (Type II).

4. Oxygen Chemisorption

Table 1 shows the amount of oxygen chemisorbed on sulfided catalysts. The amounts of oxygen chemisorbed on CoMo/Al₂O₃ catalysts (Type I and II) decreased with increasing sulfiding temperature above 673 K. The amounts of oxygen chemisorbed on MoS(x)Co/Al₂O₃ catalysts (Type II) were smaller than those of CoMo/Al₂O₃ catalysts (Type I).

5. Activity Test

Thiophene HDS actvity of CoMo/Al₂O₃ catalyst was shown in Table 2. The HDS activities of CoMo/Al₂O₃ catalysts (Type I and

Table 1. The amount of oxygen chemisorbed on CoMo/Al₂O₃ catalysts sulfided at various temperatures

Catalyst	Temperature (K)	The amount of O₂ chemisorbed (μmol/gcat)
CoMo/Al₂O₃ (Type I)	573	103.1
	673	109.7
	773	95.7
	873	89.0
	1073	48.6
MoS(673)Co/Al₂O₃ (Type II)	673	103.4
MoS(773)Co/Al₂O₃ (Type II)	773	86.3
MoS(873)Co/Al₂O₃ (Type II)	873	69.1
MoS(973)Co/Al₂O₃ (Type II)	973	47.1
MoS(1073)Co/Al₂O₃ (Type II)	1073	33.5

Table 2. Thiophene HDS activities of CoMo/Al₂O₃ catalysts sulfided at various temperatures

Catalyst	Temperature (K)	The amount of O₂ chemisorbed (μmol/gcat)
CoMo/Al₂O₃ (Type I)	673	100.5
	773	88.9
	873	67.7
	973	53.2
	1073	35.9
MoS(673)Co/Al₂O₃ (Type II)	673	124.8
MoS(773)Co/Al₂O₃ (Type II)	773	107.2
MoS(873)Co/Al₂O₃ (Type II)	873	86.9
MoS(973)Co/Al₂O₃ (Type II)	973	68.3
MoS(1073)Co/Al₂O₃ (Type II)	1073	53.4

*Activity is based on the consumption of thiophene.

II) decreased with increasing sulfiding temperature. The HDS activities of MoS(x)Co/Al₂O₃ catalysts (Type II) were higher at the same sulfiding temperature than those of CoMo/Al₂O₃ catalysts (Type I).

DISCUSSION

1. The Properties of CoMo/Al₂O₃ Catalyst

There have been many reports about the role of the interaction between Mo and support in HDS catalyst. TPS of Mo/Al₂O₃ sample showed some informations about the interaction between Mo and alumina. As shown in Fig. 1, there were two regions in which H₂S was consumed below 573 K (region I) and above 673 K (region II), respectively. H₂S consumption in region I denoted the replacement of oxygen between Mo (Mo-O-Mo) or terminal oxygen of Mo oxide (Mo=O) with sulfur while H₂S consumption in region II denoted the replacement of oxygen strongly bonded to Mo (Mo-O-Al) with sulfur [Scheffer et al., 1988; Arnoldy et al., 1985a]. This suggestion can explain that there was no H₂S consumption in region II in TPS of Mo/SiO₂ or Mo/C [Scheffer et al., 1988] in which weak interaction between Mo and support exists. TPS spectra of Mo/Al₂O₃ sulfided at various temperatures and air-contacted at room temperature showed that the amount of H₂S consumed in region II decreased. The decrease in H₂S consumption in region II might be explained as follows. Oxygen

which is weakly bonded to Mo such as terminal oxygen bonded to Mo (Mo=O) or oxygen between Mo (Mo-O-Mo) could be easily exchanged by sulfur and a part of oxygen such as Al-O-Mo is exchanged by sulfur [Scheffer et al., 1988]. When sulfided Mo /Al₂O₃ catalyst is exposed to air, sulfur species associated with Mo sulfide structure could be replaced with oxygen in air. However, Mo-O-Al bondings destroyed during sulfidation cannot be restored by the contact with air. Raman study suggested that the sulfur species associated with Mo sulfide structure could be substituted by oxygen when exposed to air and finally the microcrystalline or bulk MoO₃ are formed [Schrader and Cheng, 1983]. As a result, the amount of molybdate strongly interacting with alumina in Mo/Al₂O₃ catalyst sulfided and air-contacted at room temperature was less than that in Mo/Al₂O₃ catalyst calcined only. The replacement of sulfur species associated with Mo sulfide structure with oxygen leaves sulfur species on the surface of Mo/Al₂O₃ catalyst sulfided and air-contacted at room temperature. This sulfur species contribute to massive production of H₂S between 500 K and 600 K.

The intensity of ESR band (II) (g=2.01) in MoS(673)Co/Al₂O₃ catalyst (Type II) was stronger than that in CoMo/Al₂O₃ catalyst (Type I) as shown in Fig. 5(a) and (b). The increase in the intensity of ESR band (II) denoting the sulfur species associated with alumina, suggests the regeneration of free alumina surface. The regeneration of free alumina surface is also confirmed by the decrease in the intensity of ESR band (I) (g=1.93) assigned to Mo⁺⁵ interacting with alumina. The decrease in the interaction between Mo and alumina facilitates the formation of 2 or 3-dimensional crystalline Mo sulfide in MoS(x)Co/Al₂O₃ catalysts (Type II) as shown in XRD spectra. The formation of large crystalline Mo sulfide results in the decrease in the dispersion of Mo in MoS(x)Co/Al₂O₃ catalyst (Type II), which is confirmed by oxygen chemisorption result (Table 1) that the amounts of oxygen chemisorbed on MoS(x)Co/Al₂O₃ catalysts (Type II) were lower than those on CoMo/Al₂O₃ catalysts (Type I).

2. Activity Test

Thiophene HDS activities of MoS(x)Co/Al₂O₃ catalysts (Type II) were higher than those of CoMo/Al₂O₃ catalysts (Type I) as shown in Table 2. The change in the interaction between Mo and alumina may influence HDS activity. Two types of synergic phase exist according to the interaction between synergic phase and alumina [Candia et al., 1984a, b]. Synergic phase weakly interacting with support (Co-Mo-S II) has higher intrinsic HDS activity than synergic phase strongly interacting with support (Co-Mo-S I). The weaker intensity of ESR band (I) and the smaller amount of H₂S consumed in region II in MoS(x)Co/Al₂O₃ catalysts (Type II) suggest that the formation of Co-Mo-S II is favored in MoS(x)Co/Al₂O₃ catalysts (Type II).

When aqueous cobalt nitrate solution was impregnated into alumina, the vacancy sites in alumina structure could be used to form CoAl₂O₄ [Gates et al., 1979]. Because this compound is not sulfided at mild sulfiding condition, Co in CoAl₂O₄ may not be used to form synergic phase [Arnoldy et al., 1985b]. However, Co in MoS(x)Co/Al₂O₃ catalysts (Type II) has a greater chance to be bonded to Mo phase because the sulfidation of MoO₃/Al₂O₃ presulfided the alumina to remove vacant sites [Derouane et al., 1986; Okamoto et al., 1986]. The intensity of ESR band (IV) in MoS(x)Co/Al₂O₃ catalyst (Type II) became stronger than that in CoMo/Al₂O₃ catalyst (Type I) when sulfided at 673 K. Since ESR band (IV) is known to be related to synergic phase having higher

HDS activity [Derouane et al., 1986], the greater amount of synergic phase in MoS(x)Co/Al$_2$O$_3$ catalyst (Type II) contributes to higher HDS activity. When sulfided at 1073 K, the intensity of ESR band (V) due to cobalt sulfide in MoS(1073)Co/Al$_2$O$_3$ catalysts (Type II) was stronger than that in CoMo/Al$_2$O$_3$ catalyst (Type I), indicating the large amount of Co to be associated with Mo sulfide structure. Also the formation of CoMoO$_4$ to be inactive for HDS reaction is suppressed when Co was impregnated into sulfided Mo/Al$_2$O$_3$ [de Beer et al., 1976b] and sulfided Mo/SiO$_2$ [Gates et al., 1979].

CONCLUSION

The HDS activity of CoMo/Al$_2$O$_3$ catalyst prepared by impregnating aqueous cobalt nitrate solution into sulfided Mo/Al$_2$O$_3$ was higher than that of CoMo/Al$_2$O$_3$ catalyst prepared by impregnating aqueous cobalt nitrate solution into pre-calcined Mo/Al$_2$O$_3$. The weaker interaction between Mo and alumina and the increase in the amount of synergic phase denoted by ESR band (g=2.12) contribute to higher HDS activity of CoMo/Al$_2$O$_3$ catalyst prepared by impregnating aqueous cobalt nitrate solution into sulfided Mo/Al$_2$O$_3$.

ACKNOWLEDGEMENTS

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