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# 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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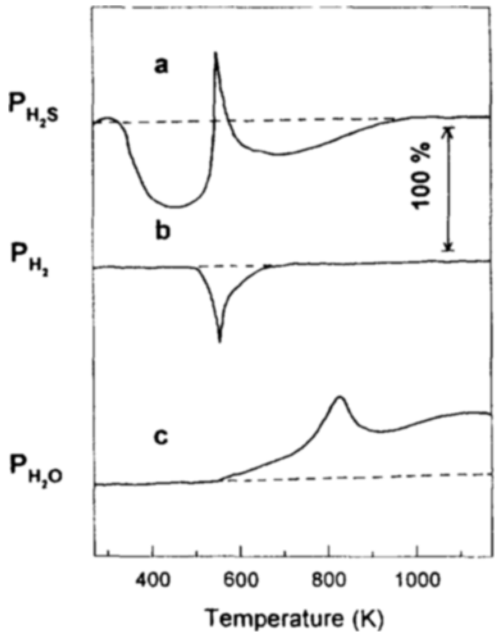

**Fig. 1. Typical patterns of TPS of calcined Mo catalyst.**
(a) $H_2S$, (b) $H_2$ and (c) $H_2O$

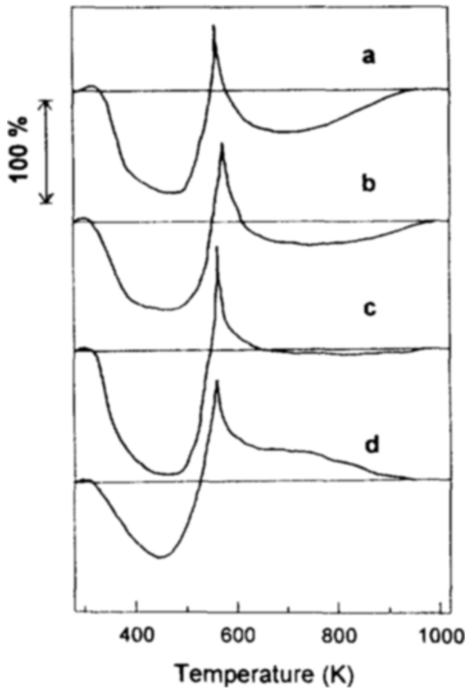

**Fig. 2. TPS patterns ($H_2S$) of $Mo/Al_2O_3$ sample.**
(a) calcined $Mo/Al_2O_3$, (b) $Mo/Al_2O_3$ sulfided at 673 K and contacted with air at room temperature, (c) $Mo/Al_2O_3$ sulfided at 873 K and contacted with air at room temperature, and (d) $Mo/Al_2O_3$ sulfided at 1073 K and contacted with 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 $N_2$. 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 $N_2$ for 0.5 h, then sulfided with a mixed flow (40 $cm^3$/min) of 10% $H_2S$ (Matheson CP grade) and 90% $H_2$ (Matheson UHP grade) for 2 h. Sulfided catalyst was flushed with $N_2$ 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 $6.55\times10^{-5}$ mol/min and the mole ratio of $H_2$/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 $Mo/Al_2O_3$ are shown in Fig. 1. There are two regions of $H_2S$ consumption: below 500 K (region I) and above 600 K (region II). $H_2S$ production accompanied by a $H_2$ consumption occurred between 500 K and 600 K. $H_2O$ 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 $H_2O$ production and $H_2S$ consumption occur simultaneously [Arnoldy et al., 1985a] and that $H_2O$ production occurs after the signal of $H_2S$ consumption [Stuchly et al., 1987]. The $H_2O$ signal which remained above 950 K without a concurrent change in the $H_2S$ and $H_2$ 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 $H_2S$ during stabilization at room temperature. The $H_2S$ adsorbed on the Mo catalyst desorbed below 373 K without $H_2O$ production. Fig. 2 showed TPS spectra of $Mo/Al_2O_3$ sample sulfided at various temperatures and contacted with air at room temperature. The amount of $H_2S$ consumed in region II was much less in $Mo/Al_2O_3$ sample sulfided and contacted with air than in $Mo/Al_2O_3$ sample calcined only. And the amount of $H_2S$ consumption decreased with increasing sulfiding temperature. And the amount of $H_2S$ production increased in $Mo/Al_2O_3$ sample sulfided and air-contacted.

### 2. XRD

XRD patterns of $CoMo/Al_2O_3$ sulfided at 873 K and 1073 K are shown in Fig. 3. XRD pattern due to the crystalline Mo sulfide was not found in $CoMo/Al_2O_3$ 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 $MoS(873)Co/Al_2O_3$ catalyst (Type II) at 873 K, XRD pattern arising from the crystalline Mo sulfide appeared at $2\theta=33°$. In $MoS(1073)Co/Al_2O_3$ 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 $g=1.93$

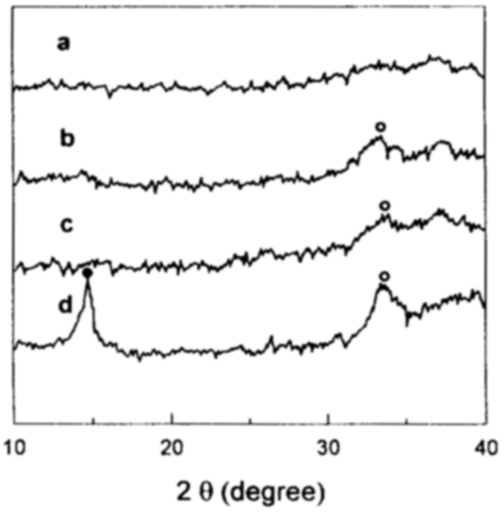

**Fig. 3. XRD spectra for CoMo/$Al_2O_3$ catalysts sulfided at various temperatures.**
(a) CoMo/$Al_2O_3$ (Type I) sulfided at 873 K, (b) CoMo/$Al_2O_3$ (Type I) sulfided at 1073 K, (c) MoS(873)Co/$Al_2O_3$ sulfided at 873 K, and (d) MoS(1073)Co/$Al_2O_3$ sulfided at 1073 K. (○) (100) plane of the crystalline molybdenum sulfide and (●) (002) plane of the crystalline molybdenum sulfide.

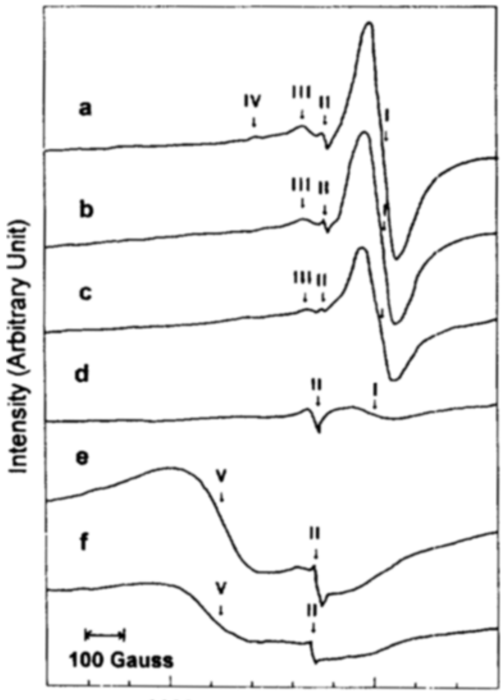

**Fig. 4. ESR spectra for CoMo/$Al_2O_3$ catalysts (Type I) sulfided at various temperatures.**
(a) 673 K, (b) 773 K, (c) 873 K, (d) 973 K, (e) 1073 K, and (f) Co/$Al_2O_3$ sulfided at 1073 K.

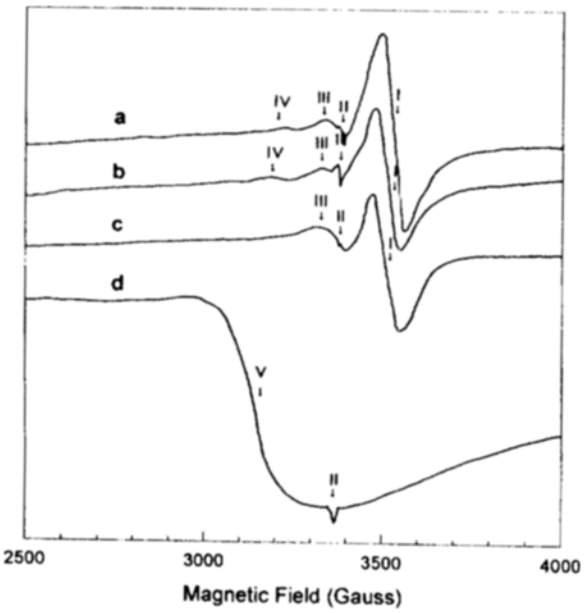

**Fig. 5. ESR spectra for CoMo/$Al_2O_3$ catalysts (Type II) sulfided at various temperatures.**
(a) CoMo/$Al_2O_3$ (Type I) sulfided at 673 K, (b) MoS(673)Co/$Al_2O_3$ sulfided at 673 K, (c) MoS(873)Co/$Al_2O_3$ sulfided at 873 K, and (d) MoS(1073)Co/$Al_2O_3$ sulfided at 1073 K.

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 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/$Al_2O_3$ 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/$Al_2O_3$ at 1073 K [Fig. 4(f)]. When sulfiding MoS(673)Co/$Al_2O_3$ 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/$Al_2O_3$ catalyst (Type II) was stronger than that in CoMo/$Al_2O_3$ catalyst (Type I). When sulfided at 1073 K, the intensity of ESR band (V) in MoS(1073)Co/$Al_2O_3$ catalyst (Type II) was stronger than that in CoMo/$Al_2O_3$ catalyst (Type I) and ESR band (I) completely disappeared in MoS(1073)-Co/$Al_2O_3$ catalyst (Type II).

### 4. Oxygen Chemisorption

Table 1 shows the amount of oxygen chemisorbed on sulfided catalysts. The amounts of oxygen chemisorbed on CoMo/$Al_2O_3$ catalysts (Type I and II) decreased with increasing sulfiding temperature above 673 K. The amounts of oxygen chemisorbed on MoS(x)Co/$Al_2O_3$ catalysts (Type II) were smaller than those of CoMo/$Al_2O_3$ catalysts (Type I).

### 5. Activity Test

Thiophene HDS actvity of CoMo/$Al_2O_3$ catalyst was shown in Table 2. The HDS activities of CoMo/$Al_2O_3$ catalysts (Type I and

**Table 1. The amount of oxygen chemisorbed on CoMo/$Al_2O_3$ catalysts sulfided at various temperatures**

| Catalyst | Temperature (K) | The amount of $O_2$ chemisorbed (μmol/gcat) |
|---|---|---|
| CoMo/$Al_2O_3$ (Type I) | 573 | 103.1 |
| | 673 | 109.7 |
| | 773 | 95.7 |
| | 873 | 89.0 |
| | 1073 | 48.6 |
| MoS(673)Co/$Al_2O_3$ (Type II) | 673 | 103.4 |
| MoS(773)Co/$Al_2O_3$ (Type II) | 773 | 86.3 |
| MoS(873)Co/$Al_2O_3$ (Type II) | 873 | 69.1 |
| MoS(973)Co/$Al_2O_3$ (Type II) | 973 | 47.1 |
| MoS(1073)Co/$Al_2O_3$ (Type II) | 1073 | 33.5 |

**Table 2. Thiophene HDS activities of CoMo/$Al_2O_3$ catalysts sulfided at various temperatures**

| Catalyst | Temperature (K) | The amount of $O_2$ chemisorbed (μmol/gcat) |
|---|---|---|
| CoMo/$Al_2O_3$ (Type I) | 673 | 100.5 |
| | 773 | 88.9 |
| | 873 | 67.7 |
| | 973 | 53.2 |
| | 1073 | 35.9 |
| MoS(673)Co/$Al_2O_3$ (Type II) | 673 | 124.8 |
| MoS(773)Co/$Al_2O_3$ (Type II) | 773 | 107.2 |
| MoS(873)Co/$Al_2O_3$ (Type II) | 873 | 86.9 |
| MoS(973)Co/$Al_2O_3$ (Type II) | 973 | 68.3 |
| MoS(1073)Co/$Al_2O_3$ (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/$Al_2O_3$ catalysts (Type II) were higher at the same sulfiding temperature than those of CoMo/$Al_2O_3$ catalysts (Type I).

## DISCUSSION

### 1. The Properties of CoMo/$Al_2O_3$ Catalyst

There have been many reports about the role of the interaction between Mo and support in HDS catalyst. TPS of Mo/$Al_2O_3$ sample showed some informations about the interaction between Mo and alumina. As shown in Fig. 1, there were two regions in which $H_2S$ was consumed below 573 K (region I) and above 673 K (region II), respectively. $H_2S$ 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 $H_2S$ 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 $H_2S$ consumption in region II in TPS of Mo/$SiO_2$ or Mo/C [Scheffer et al., 1988] in which weak interaction between Mo and support exists. TPS spectra of Mo/$Al_2O_3$ sulfided at various temperatures and air-contacted at room temperature showed that the amount of $H_2S$ consumed in region II decreased. The decrease in $H_2S$ 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/$Al_2O_3$ 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 $MoO_3$ are formed [Schrader and Cheng, 1983]. As a result, the amount of molybdate strongly interacting with alumina in Mo/$Al_2O_3$ catalyst sulfided and air-contacted at room temperature was less than that in Mo/$Al_2O_3$ catalyst calcined only. The replacement of sulfur species associated with Mo sulfide structure with oxygen leaves sulfur species on the surface of Mo/$Al_2O_3$ catalyst sulfided and air-contacted at room temperature. This sulfur species contribute to massive production of $H_2S$ between 500 K and 600 K.

The intensity of ESR band (II) (g=2.01) in MoS(673)Co/$Al_2O_3$ catalyst (Type II) was stronger than that in CoMo/$Al_2O_3$ 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/$Al_2O_3$ 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/$Al_2O_3$ catalyst (Type II), which is confirmed by oxygen chemisorption result (Table 1) that the amounts of oxygen chemisorbed on MoS(x)Co/$Al_2O_3$ catalysts (Type II) were lower than those on CoMo/$Al_2O_3$ catalysts (Type I).

### 2. Activity Test

Thiophene HDS activities of MoS(x)Co/$Al_2O_3$ catalysts (Type II) were higher than those of CoMo/$Al_2O_3$ 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 $H_2S$ consumed in region II in MoS(x)Co/$Al_2O_3$ catalysts (Type II) suggest that the formation of Co-Mo-S II is favored in MoS(x)Co/$Al_2O_3$ catalysts (Type II).

When aqueous cobalt nitrate solution was impregnated into alumina, the vacancy sites in alumina structure could be used to form $CoAl_2O_4$ [Gates et al., 1979]. Because this compound is not sulfided at mild sulfiding condition, Co in $CoAl_2O_4$ may not be used to form synergic phase [Arnoldy et al., 1985b]. However, Co in MoS(x)Co/$Al_2O_3$ catalysts (Type II) has a greater chance to be bonded to Mo phase because the sulfidation of $MoO_3$/$Al_2O_3$ 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/$Al_2O_3$ catalyst (Type II) became stronger than that in CoMo/$Al_2O_3$ 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/$Al_2O_3$ 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/$Al_2O_3$ catalysts (Type II) was stronger than that in CoMo/$Al_2O_3$ 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/$Al_2O_3$ [de Beer et al., 1976b] and sulfided Mo/$SiO_2$ [Gates et al., 1979].

## CONCLUSION

The HDS activity of CoMo/$Al_2O_3$ catalyst prepared by impregnating aqueous cobalt nitrate solution into sulfided Mo/$Al_2O_3$ was higher than that of CoMo/$Al_2O_3$ catalyst prepared by impregnating aqueous cobalt nitrate solution into pre-calcined Mo/$Al_2O_3$. 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/$Al_2O_3$ catalyst prepared by impregnating aqueous cobalt nitrate solution into sulfided Mo/$Al_2O_3$.

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