

## CHAPTER II

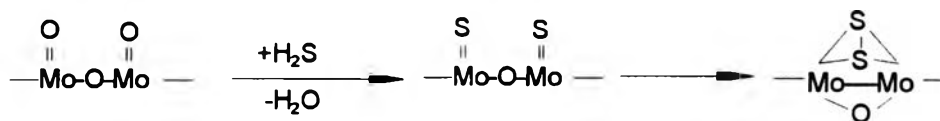
### HISTORICAL REVIEW

#### 2.1 Background

Catalysts in hydrodesulfurization process have been extensively studied. Much of the efforts have been focused on the nature of the active sites in the cobalt-molybdenum/alumina system. A better understanding of their functions will provide fundamental information for fabricating more resistant catalysts for heavy residues and synthetic-derived feeds.

It has been known that the HDS catalysts are active when sulfided. However, the type of oxide species before sulfiding has a great effect on the final sulfided species. Normally, the catalysts are reduced with hydrogen to their lowest oxidation state. Patterson, et al. (1976) measured the reduction of Mo on alumina support with time. It shows that Mo(V) is an intermediate in the reduction of Mo(VI) to Mo(IV). Approximately 35% of Mo remains present as Mo(V) at equilibrium. Muijsers, et al. (1995) suggested that sulfiding of MoO<sub>3</sub>/SiO<sub>2</sub>/Si(100) catalyst system, molybdenum was initially in the 6<sup>+</sup> state then converted through a Mo<sup>5+</sup> intermediate to the eventual Mo<sup>4+</sup> present in MoS<sub>2</sub>. They proposed the mechanism of O-S exchange followed by and Mo-S redox process during sulfidation by H<sub>2</sub>S/H<sub>2</sub> over MoO<sub>3</sub>-type precursor.

The proposed mechanisms is written as:



Duchet, et al. (1983) showed that the amorphous carbon supported catalysts have a fair amount of adsorption sites for oxides of Mo and W species. The interaction of the oxides with amorphous carbon is strong enough to create a high degree of dispersion in the catalyst precursor and weak enough not to hamper the formation of the actual active sulfide phase. Their XPS results also showed the presence of sulfur ions with a valence state of -1 such as single  $\text{S}^{1-}$  ions or  $(\text{S-S})^{2-}$  pairs, instead of -2. They suggested that these low valence sulfur ions are more reactive with thiophene during the HDS reaction.

Topsoe and Topsoe (1993) studied the coverage of molybdenum on alumina by using the disappearance of surface hydroxyl group. The FT-IR results had shown that the free hydroxyl groups decreased as molybdenum loading increased due to the interaction of molybdenum with the surface. The OH band disappeared at 12% Mo loading, indicating the monolayer coverage of the surface OH group. Sulfided catalysts showed the regenerated OH group on the surface, caused by the breaking of Mo-O-Al bond during sulfiding. From OH/Mo ratio calculated, they suggested that at low Mo loading the molybdenum coordination was tetrahedral, since it bonded to the alumina surface via two oxygen atoms giving a high dispersion of Mo on the surface. While octahedrally coordinated molybdenum atoms are more extensively bridged to each other.

Wang and Hall (1982) studied on the equilibrium adsorption technique with different catalyst systems. The loading of the support was found not to depend on the solution concentration. The loading of the anion was a strongly dependent on the pH, which reflected the isoelectric point of the support surface. Titania support showed the highest Mo loading over a wide range of pH compared to silica gel and  $\gamma$ -alumina. They suggested that the monomeric tetrahedral molybdenum was formed on the catalysts prepared at pH of 8.9 while those made at lower pH yielded polymeric octahedral species. This equilibrium adsorption technique showed a good dispersion of metal compared to that of the incipient wetness technique which gave randomly distributed small clusters over the support surface.

Ng and Gulari (1985) studied the Co-Mo catalyst on  $\text{TiO}_2$  supported. They found that the surface species depended on the loading, pH of the starting solution and the method of catalyst loading. They used the equilibrium adsorption loading to obtain good dispersion of molybdenum. The coverages were calculated to be less than a monolayer for this method of preparation and the main surface species were tetrahedral molybdates with an increase of octahedrally coordinated polymeric surface species at higher loadings. The deposition of tetrahedral molybdates also preferred the pH of greater than 8, measured after calcining. Above the monolayer coverage, for  $\text{TiO}_2$ , bulk-like  $\text{MoO}_3$  formed. Compared to the alumina support, there was no formation of  $\text{MoO}_3$  on titania at submonolayer loadings even when the impregnation method of preparation was used. Moreover, the addition of cobalt to titania supported molybdenum catalysts suppressed the formation of bulk  $\text{MoO}_3$  and led to the formation of cobalt molybdate phase. The study also showed that for titania support the order of loading (Co or Mo) made no difference to the structure of catalysts after calcining. They proposed the model of Co-Mo/ $\text{TiO}_2$  system as

the bonding of molybdenum atoms to the support with oxygen bridged to the cobalt molybdates species on the surface. If  $\text{MoO}_3$  was formed (above monolayer), the cobalt molybdate layers were formed on top of polymolybdates. Webber (1995) also observed the tetrahedral Mo species at low loading and the polymeric octahedral Mo at high loading using UV-visible absorption edges of molybdenum oxide.

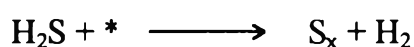
Martin, et al. (1996) studied alkaline-metal doped  $\text{MoO}_3/\text{TiO}_2$  systems, and found that the structure of undoped  $\text{MoO}_3$  was mostly octahedrally coordinated molybdenum. When doped with 1% wt Li only tetrahedrally coordinated,  $\text{MoO}_4^{2-}$ , occurred. However, Na and K- doped systems showed combination of tetrahedrally and octahedrally coordinated molybdenum. They also found that the preparation step affected the structure of the supported phase.

Ng and Gulari (1985) have shown that the low loading titania-supported catalysts which were mostly tetrahedral molybdate, were more active in HDS reaction compared to alumina-supported catalysts, and the cobalt promoter increased the activity only modestly for titania supported catalysts.

Zhang and Vasudevan (1995) compared the molybdenum sulfide catalysts prepared by reductive sulfiding of oxide to the ones prepared by decomposition of ammonium tetrathiomolybdate (ATTM). The molybdenum sulfide prepared by decomposition of ATTM showed higher hydrogenation reaction of propylene. They proposed this effect to the partial sulfidation of the conventional reductive sulfiding. Their temperature-programmed desorption (TPD) of  $\text{H}_2\text{S}$  showed a higher activity of the catalyst which had a high reduction temperature. They attributed this effect to the non stoichiometric

sulfur atoms blocking coordinatively unsaturated sites, number of anion vacancies per Mo site, at low temperature. The cobalt promotion increased HDS activity but not hydrogenation activity.

Mangnus, et al. (1995) studied on the temperature-programmed reduction (TPR) of sulfided HDS catalysts. The various transition metals were impregnated on  $\gamma$ -alumina support. Four different sulfur species were determined using TPR, which are stoichiometric sulfur, non stoichiometric sulfur or  $S_x$ , S-H groups and adsorbed  $H_2S$ . Because of the  $H_2$  rich atmosphere in HDS process, the reduction of stoichiometric sulfur may take place. The non-stoichiometric sulfur,  $S_x$ , is formed by dissociation of  $H_2S$  on coordinatively unsaturated sites. This process occurs during the purging of catalysts. The desorption rate of  $H_2$  is much faster than that of  $H_2S$ , resulting in an increase of the  $H_2S/H_2$  ratio in the pores of the catalysts. The dissociation of  $H_2S$  occurs as follows:



where \* = coordinatively unsaturated sites

This  $S_x$  species were shown in the low temperature range of TPR. They also found a weak correlation between the thiophene HDS activity and the catalyst reduction temperature.

Okamoto, et al. (1980) found that hydrogenation and HDS activities of sulfided  $MoO_3/Al_2O_3$  catalysts depended on sulfidation degrees of molybdenum regardless of the molybdenum content, calcination temperature, and sulfidation conditions. For low-sulfur content catalysts ( $S/Mo < 1$ ), the

relative activity for hydrogenation to HDS was constant, implying that only one kind of molybdenum species, which is active for both reactions, is present. They suggested that two-dimensional  $\text{MoS}_2$  was initially formed and subsequently transformed to three-dimensional  $\text{MoS}_2$  microcrystals by further sulfidation of the catalysts, accompanying the sintering of molybdenum.

Patterson, et al. (1976) used an X-ray photoelectron spectroscopy (XPS) to study the surface reactions of a commercial  $\text{CoMo}/\text{Al}_2\text{O}_3$  catalyst. The reduction of catalyst in  $\text{H}_2$  produced a mixture of molybdenum oxide states;  $\text{Mo(VI)}$ ,  $\text{Mo(V)}$ , and  $\text{Mo(IV)}$ . Thiophene adsorption occurred on the fired catalysts contacted with thiophene in an inert atmosphere. In contrast, the fired catalysts with pre-reduction with  $\text{H}_2$  showed both thiophene adsorption and desulfurization. In the thiophene with hydrogen atmosphere, fired, pre-reduced catalysts sulfided to a lesser extent than fired catalysts. However, the fired, pre-reduced catalysts had a higher HDS activity and maintained the activity higher for a long period of time. The molybdenum on catalyst was effectively sulfided in either thiophene/ $\text{H}_2$  or  $\text{H}_2\text{S}/\text{H}_2$ , but no completed sulfiding was observed.

Portela, et al. (1995) studied the  $\text{CoMo}/\text{Al}_2\text{O}_3$  catalysts sulfided by different procedures. They concluded that the sulfidation of the catalysts with  $\text{H}_2\text{S}$  alone led to a decrease of the coverage of the support by the molybdenum sulfide phase which can be attributed to a large crystallite diameter. The pre-reduction with  $\text{H}_2$  of the catalysts led to a generalized decrease of the amount of surface sulfur, attributed to the difficult sulfidation of  $\text{MoO}_2$  formed during the reduction step of the catalysts. The post-treatment of sulfided catalysts did not cause any changes as deep as the pretreatment did. Nevertheless, the amount of surface sulfur increased or decreased as hydrogen sulfide or hydrogen were used, respectively. The incorporation of Co into the Mo

catalysts led to an increase of the dispersion of the Mo to its higher sensitivity to sulfiding procedures.

Support materials also play an important role on the catalyst activity. Besides the large surface area, the interaction of metal with support is of important. Topsoe, et al. (1979) found that support materials such as alumina, silica, and carbon, had a significant influence on the final structure of catalysts due to their different strengths of interaction. Duchet, et al. (1983) studied supported sulfided catalysts and found that the thiophene HDS activity per mole of Mo increased in the order of Mo/g-Al<sub>2</sub>O<sub>3</sub>, Mo/SiO<sub>2</sub> and Mo/C respectively. They explained that the difference in activity was due to different degrees of interaction, the stronger the interaction, the lower the activity. Muralidhar, et al. (1984) attributed the high HDS activity of alumina-supported catalysts to a stronger interaction with the alumina, thus, better dispersion in oxidized and sulfided state.

Okazaki, et al. (1981) found that the activity of supported moly-oxide catalysts for the reduction of NO with NH<sub>3</sub> followed the order of TiO<sub>2</sub>, ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> respectively. The activities of MoO<sub>x</sub>-TiO<sub>2</sub> and MoO<sub>x</sub>-ZrO<sub>2</sub> were found to increase when a small amount of SO<sub>4</sub><sup>2-</sup> was added. At high reaction temperature, TiO<sub>2</sub> showed almost 100% NO conversion if it included a small amount of SO<sub>4</sub><sup>2-</sup>. The positive effect of SO<sub>4</sub><sup>2-</sup> on the activity of MoO<sub>3</sub>-TiO<sub>2</sub> and the activity change with the change of Mo content were caused by the acidity change on the surface of the catalyst.

## 2.2 Research Objective

The purpose of this work was to study the effect of sulfidation level to the activity and selectivity of the catalysts. The objective could be divided into three experimental parts. The first part was the catalyst preparation. The catalysts were prepared by equilibrium adsorption technique and impregnation technique. Molybdenum on titania was used as the catalysts in this work. The activity and selectivity of these catalysts would be compared. The second part was the characterization of sulfided catalysts. The last part was to find the relation among an amount of thiophene in feed, sulfidation level, activity and selectivity of the catalysts.