CHAPTER IV
RESULTS AND DISCUSSION

4.1 Activity and Selectivity Studies

The effect of thiophene composition in feed on the activities of the catalysts is shown in Figure 4.1. It can be seen that the activity of the catalysts decreased with increasing thiophene in feed. The catalyst prepared by equilibrium adsorption which had a molybdenum loading of 2.5% showed higher activity compared to the catalyst prepared by impregnation technique which had a molybdenum loading of 5%. This means that the equilibrium loading catalyst contained more active species for HDS reaction even though it had a lower Mo content. The linear decrement of the activity of impregnation catalyst implies that the increment of the C_4-products was small compared to the increment of thiophene concentration in feed. The decrease in activity of equilibrium adsorption catalyst seems to level off at about 5% thiophene feed which means the increase of C_4-products is comparable with the increase in the thiophene concentration.

Figure 4.2 illustrates the selectivities of the catalysts at various thiophene concentrations in the feed. Both catalysts give a high ratio of hydrogenation rate to hydrodesulfurization rate with increasing thiophene concentration. However, the equilibrium adsorption catalyst shows slightly higher selectivity compared to that of the impregnation catalyst. The

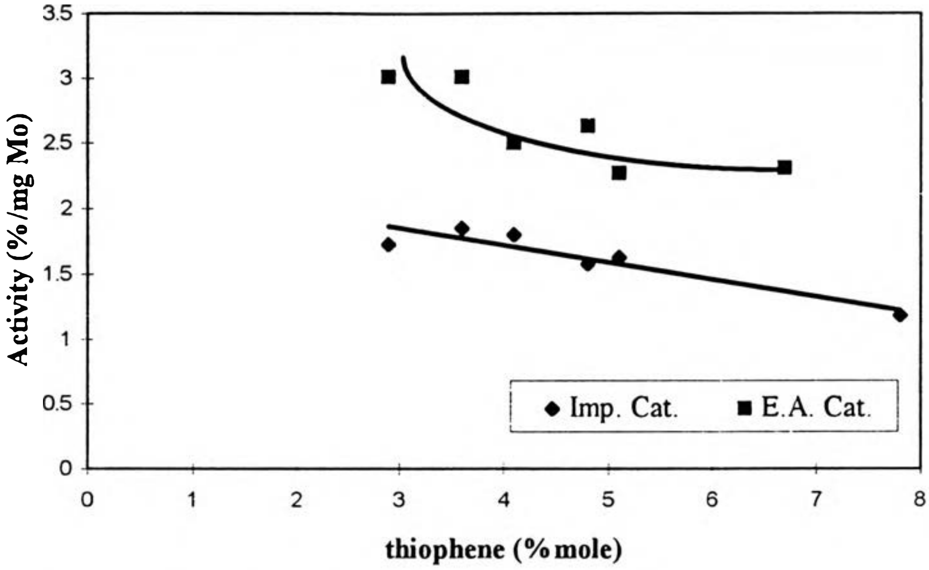


Figure 4.1 Activities of catalysts at various thiophene feedings.

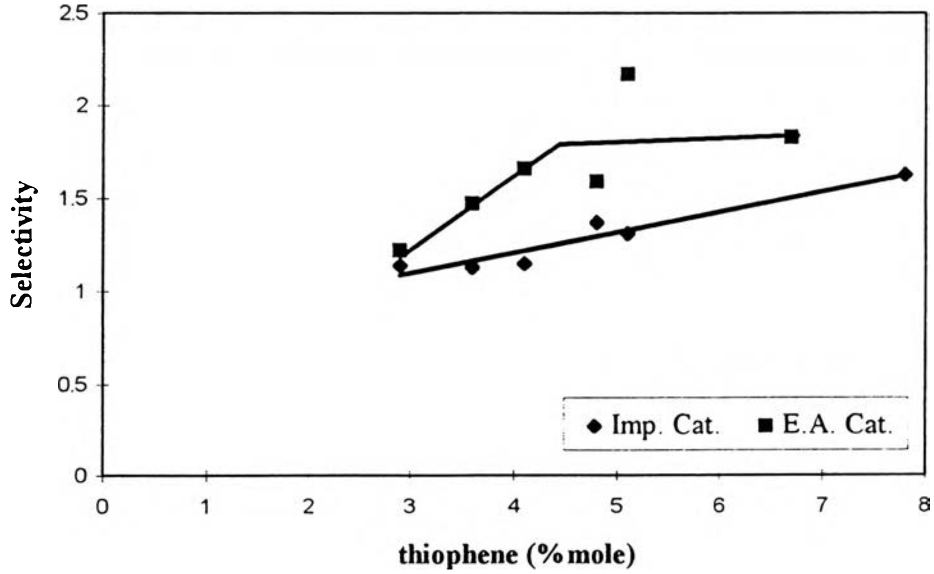
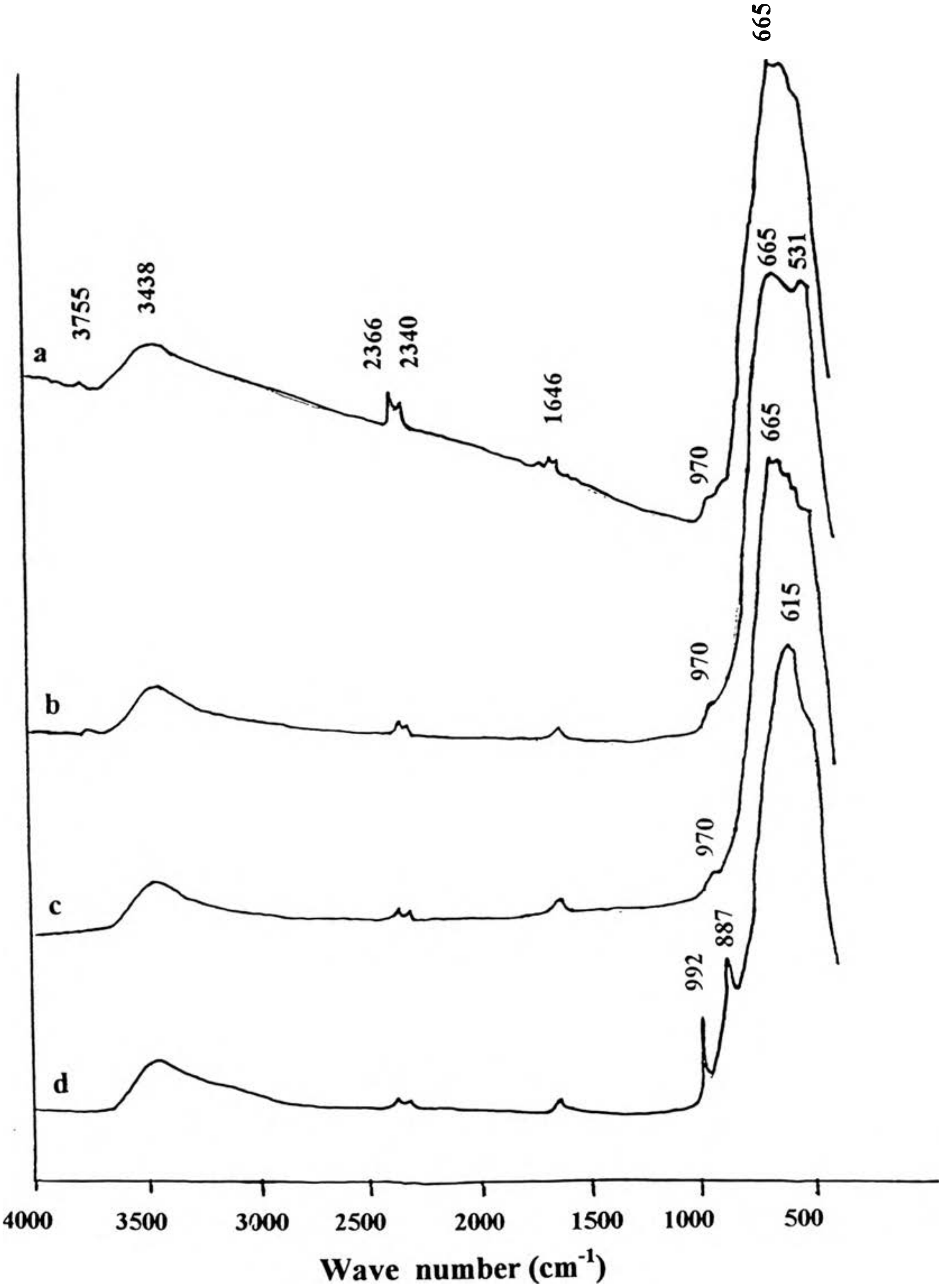


Figure 4.2 Selectivities of catalysts at various thiophene feedings.

proposed model of Okamato, et al. (1980) could explain this behavior. They suggested that at high sulfur level, the surface species formed three-dimensional MoS_2 which has lower HDS active sites compared to hydrogenation sites, resulting in the increase in selectivity. The high activity of equilibrium adsorption catalyst compared to impregnation catalyst is in agreement with Ng and Gulari (1985). Their data were obtained at 2.6% thiophene feeding (thiophene vapor at 0 °C, 1 atm) which showed higher activities for both catalysts in the magnitude of about 2. However, the selectivities were almost the same. The activity and selectivity in this work were reproducible within 5% in duplication runs.

4.2 Surface Study

The species on the catalyst surface is shown in Figure 4.3. The FT-IR absorbance spectra of fresh impregnation catalyst showed peaks at 992 and 887 cm^{-1} which pertain to bulk MoO_3 whereas the fresh equilibrium adsorption catalyst does not show the polymeric molybdenum oxides. When sulfided the peak of MoO_3 decreased, indicating that oxygen was being replaced by sulfur. The results are in agreement with Ng and Gulari (1985) in that the main surface species of the impregnation catalyst at loading above monolayer coverage contained mostly MoO_3 which is less active than tetrahedral molybdate species found in low loading equilibrium adsorption catalyst. Both sulfided catalysts showed a peak at 3755 cm^{-1} which represents an isolated hydroxyl group. This peak is absent in the fresh catalysts. This finding is in agreement with Topsoe and Topsoe (1992) that the IR peak of OH group in the region of 3755 cm^{-1} had disappeared in the oxide catalysts



a : sulfided impregnation catalyst
b : sulfided equilibrium adsorption catalyst
c : fresh equilibrium adsorption catalyst
d : fresh impregnation catalyst

Figure 4.3 The FT-IR spectra of the Mo/TiO_2 catalysts.

due to the interaction of molybdenum to the surface hydroxyl group. When sulfided, the free OH bands increased, showing that the OH group is regenerated after sulfidation of molybdenum. However, there was higher intensity of OH peak in their oxide catalysts. This may be due to the high surface OH group on the alumina support compared to that of the titania.

Raman spectra of the catalysts are compared in figure 4.4. The peaks at 520 and 643 cm^{-1} are due to the titania support. These spectra are normalized using the titania peak at 643 cm^{-1}. The sharp peaks at 820 and 996 cm^{-1} are due to the bulk-like MoO_3. Impregnation catalyst at 5% Mo contained mainly this type of molybdenum. The equilibrium adsorption, 2.5 % Mo, had small amount of MoO_3. However, there was a peak of $Mo_7O_{24}^{6-}$ at 945 cm^{-1}. When sulfided, the intensity of MoO_3 peaks decreased for both types of catalysts. Whereas, the $Mo_7O_{24}^{6-}$ peak had disappeared in equilibrium adsorption catalyst. These are due to the transformation of molybdenum oxide to molybdenum sulfide. The equilibrium adsorption showed an interesting feature: the peak at 820 cm^{-1} decreased dramatically besides the disappearance of the $Mo_7O_{24}^{6-}$ peak. This implies that the polymeric molybdate is easier to sulfide. However, a small amount of bulk-like MoO_3 in equilibrium adsorption catalyst can also be easily sulfided compared to the large peaks remaining in the impregnation catalysts.

Comparing the raman spectra of oxide catalysts with those of Ng and Gulari (1985), it is shown that the bulk-like MoO_3 peaks of the catalysts are in good agreement. However, the $Mo_7O_{24}^{6-}$ peak which showed in equilibrium adsorption catalyst, appeared in their impregnation catalysts in the whole

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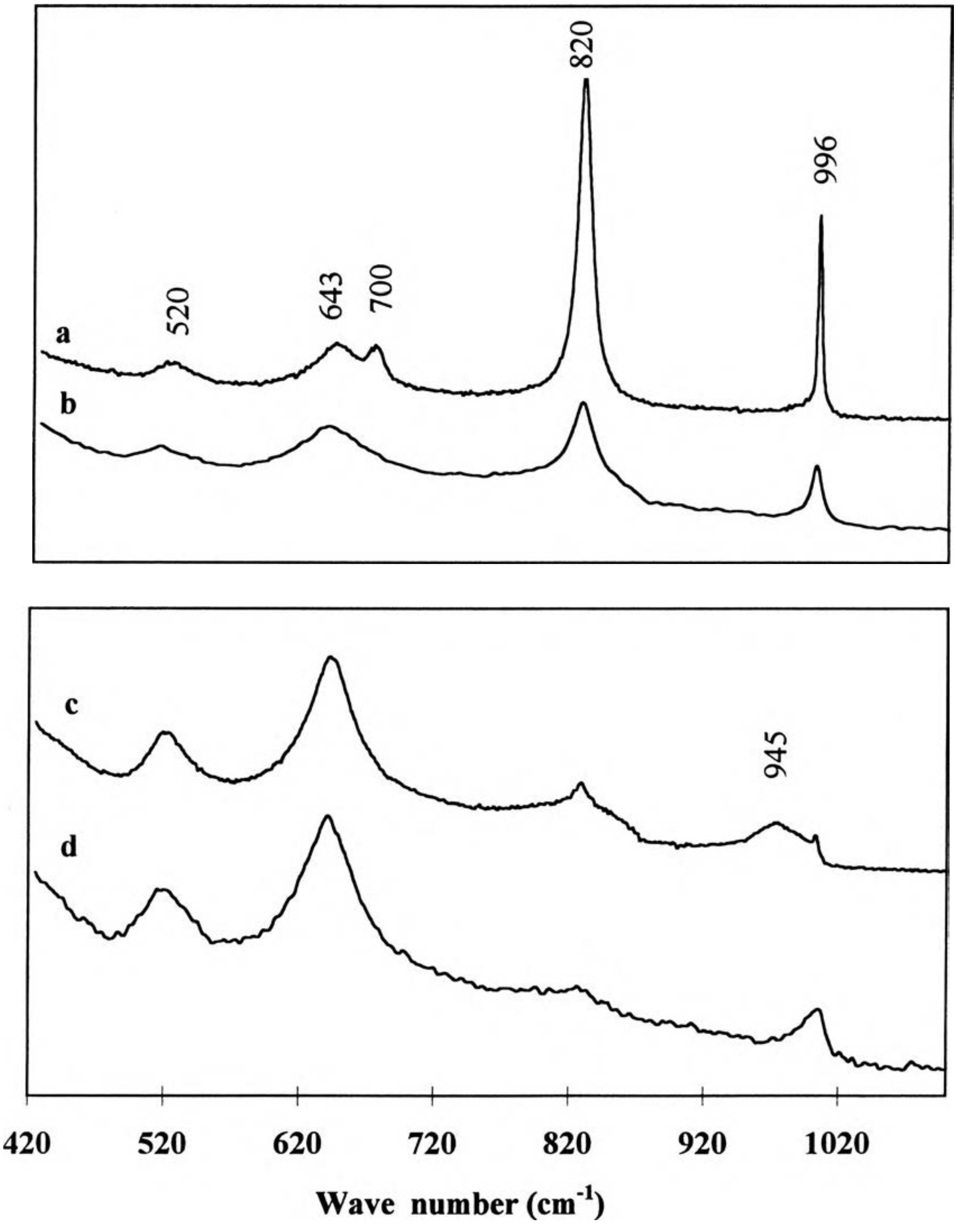

a: fresh impregnation catalyst
b: sulfided impregnation catalyst
c: fresh equilibrium adsorption catalyst
d: sulfided equilibrium adsorption catalyst

Figure 4.4 The Raman spectra of the Mo/TiO$_2$ catalysts.

range of molybdenum loading. Moreover, the small peak of impregnation catalyst, 5% Mo, at 700 cm^{-1} which may be due to the molybdenum peak in Figure 4.4, appeared in the Co-Mo catalyst system at low molybdenum loading in their raman spectra. These may be due to the change of the molybdenum coordinates when cobalt was added. It is also possible that the molybdenum coordinate in Figure 4.4 is the same as those appeared in the Co-Mo catalyst system.

The $Mo_7O_{24}^{6-}$ species found in this work is in agreement with Wang and Hall (1982) that this molybdate species is the main species in the pH range of 2 to 6 in equilibrium adsorption catalysts.

Sulfidation level of the catalysts at various compositions of thiophene is shown in Figure 4.5. It can be seen that the impregnation catalyst has a higher level of sulfur compared to the equilibrium adsorption catalyst. The sulfidation level of the impregnation catalyst varied around 1.8% while the equilibrium adsorption catalyst showed more fluctuation of the sulfidation level. The average value was 0.65%. The sulfidation value of the equilibrium adsorption catalyst is small and may be in an error range of the equipment. However, it can be seen that when the molybdenum loading was doubled (2.5% to 5%) the sulfidation level was almost doubled. Therefore, it indicates that the impregnation and equilibrium adsorption catalysts had the same stoichiometric molybdenum-sulfur ratio. However, the active species were different which can be seen from the different in activities. The data from Figure 4.5 can be converted to the atomic ratio of S/Mo, to find that it is between 0.4 and 1.2 for the equilibrium adsorption catalyst and between 0.9 and 1.3 for the impregnation catalyst. Okamoto, et al. (1980) found that the

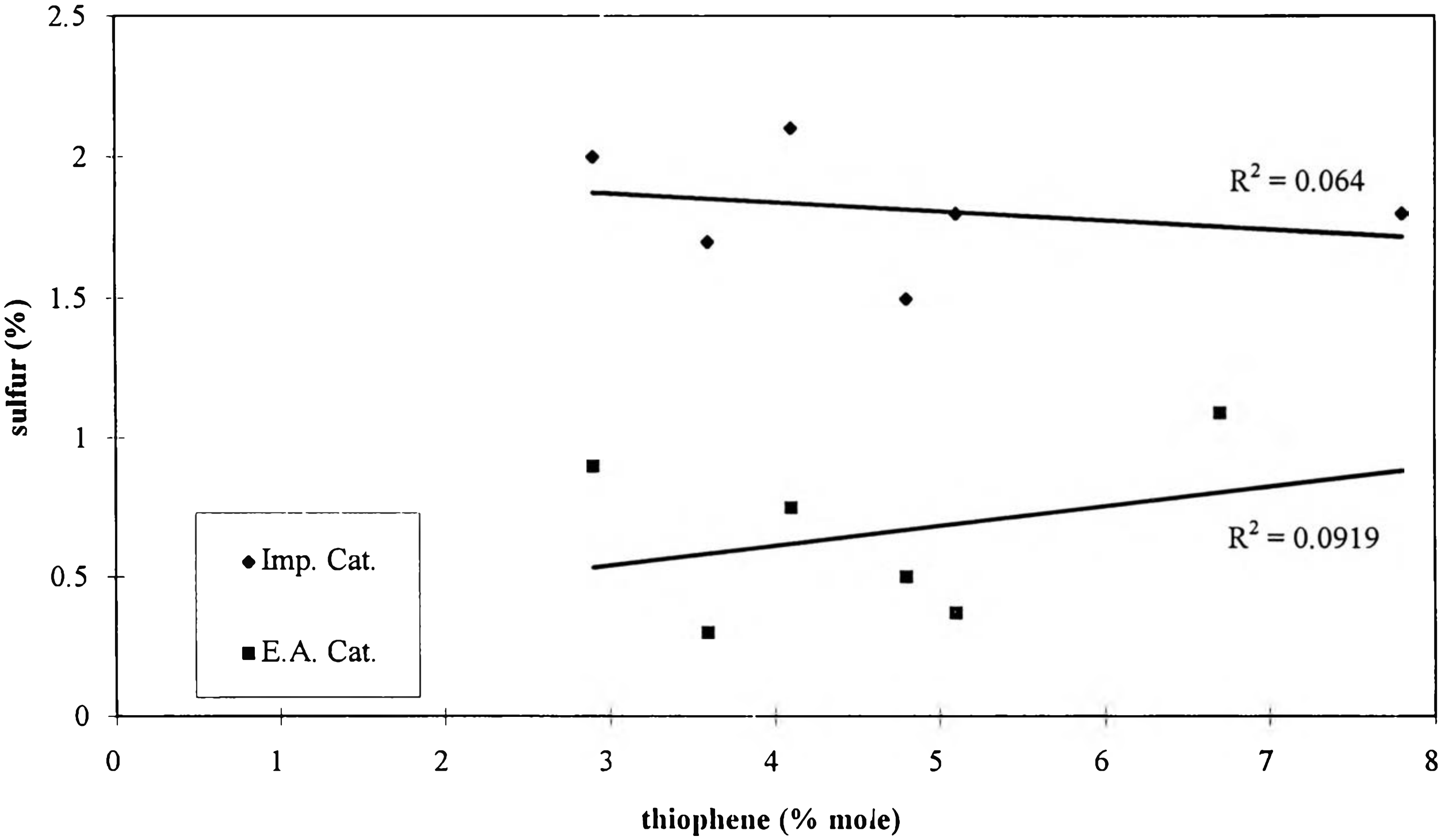

Figure 4.5 Sulfidation level of catalysts at various thiophene compositions.

atomic ratio of S/Mo at the value of unity for MoO_3/Al_2O_3, gave the highest intrinsic activity and the selectivity was in a range of 0.9 to 1.1. The selectivity in this work, Mo/TiO_2, has shown to be comparable. However, the activity is much lower which may be due to the different in operating conditions. The selectivity implies that the surface active species may be the same.

4.3 Effect of Pre-Reduction

It is known that the catalysts are active when sulfided. The normal sulfiding condition is hydrogen sulfide in hydrogen atmosphere. Figures 4.6 4.7, 4.8 and 4.9 show that the catalyst can be sulfided with thiophene in hydrogen atmosphere. However, the pre-reduction catalyst showed higher activity. It is also interesting that the selectivity of pre-reduction, no pre-reduction and post-reduction catalysts were almost the same. This implies that only one type of surface site is responsible for both reactions.

Okamoto, et al. (1980) found that at 4.8% wt MoO_3/Al_2O_3 the pretreatment with CS_2/H_2 gave higher activity compared to no pretreatment and reduction with H_2 respectively. However, the length of their pretreatment of an hour is small compared to 12 hours in this work. Therefore, it is possible that the longer H_2 reduction period would show a higher activity. With MoO_3 higher than 13%, their results appeared that the prereduction with H_2 showed an increased in activity. It is possible that at high loading, molybdenum may form the structure that is easily reduced in a short period of time. Portela, et al. (1995) suggested that the H_2 prereduction caused the formation of MoO_2

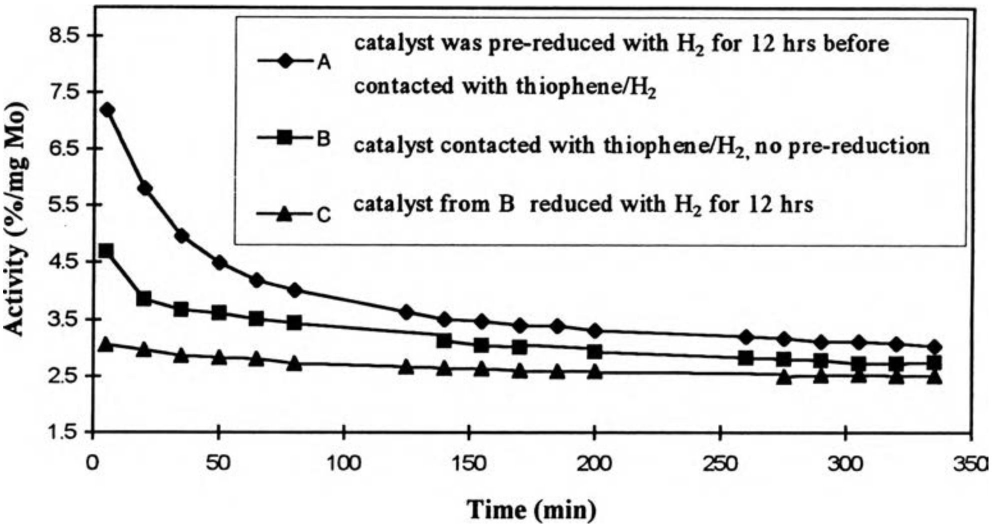

Figure 4.6 Activities of equilibrium adsorption catalysts sulfided with different conditions while keeping thiophene content at 4.8% mole.

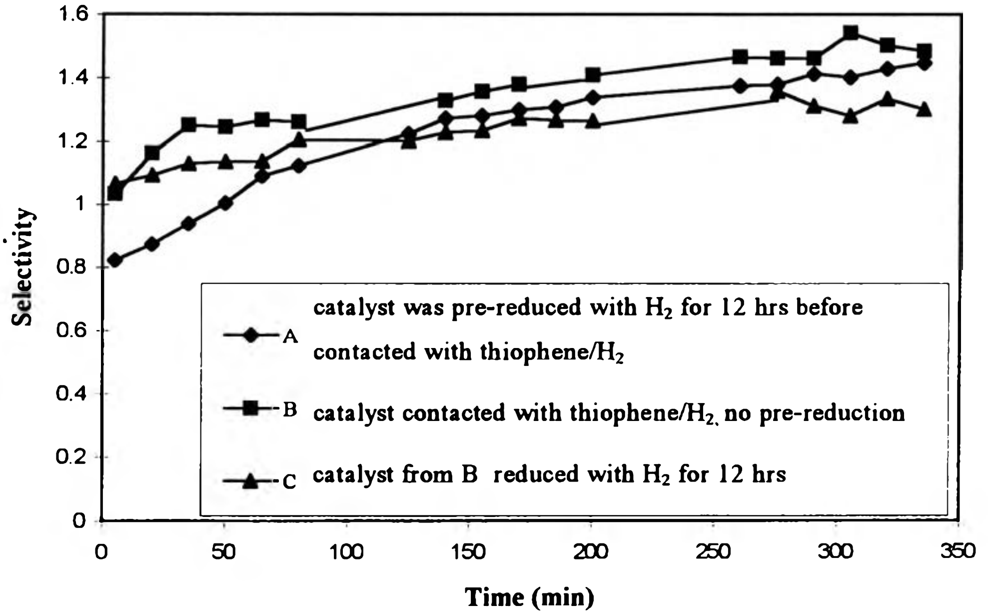

Figure 4.7 Selectivities of equilibrium adsorption catalysts sulfided with different conditions while keeping thiophene content at 4.8% mole.

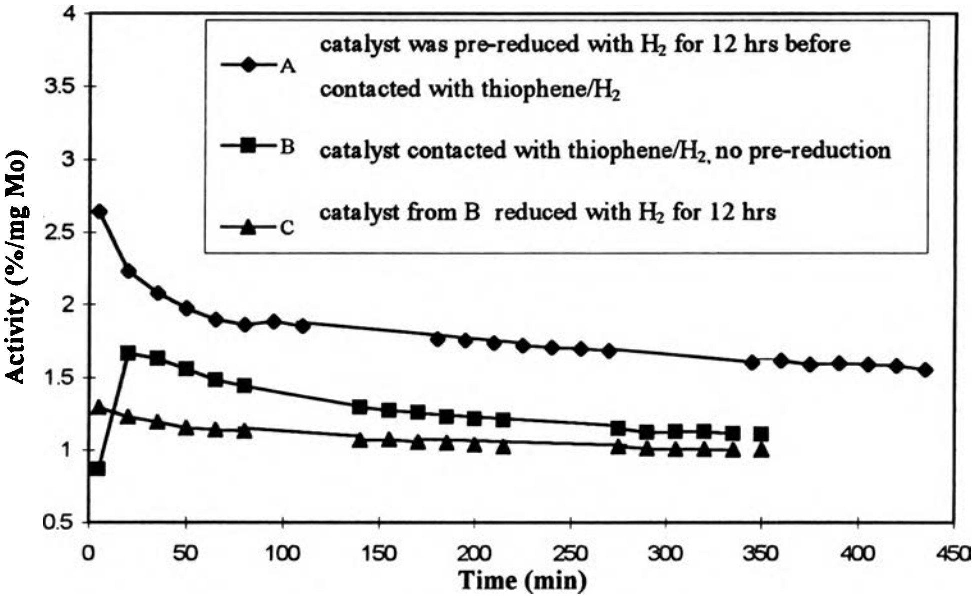

Figure 4.8 Activities of impregnation catalysts sulfided with different conditions while keeping thiophene content at 4.8% mole.

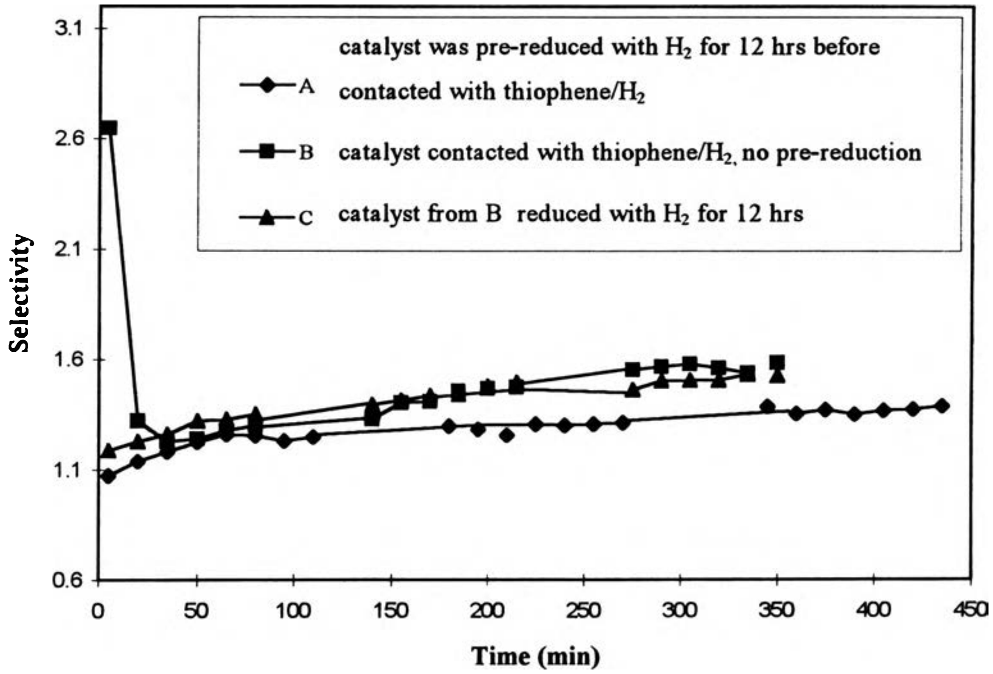

Figure 4.9 Selectivities of impregnation catalysts sulfided with different conditions while keeping thiophene content at 4.8% mole.

which is difficult to sulfiding. Their proposed cannot apply in this case. The high activities of H_2 pretreatment in this work is in good agreement with Patterson, et al. (1976). They suggested that H_2 prereduction showed higher activities and maintained the higher activities for a long period of time.

The equilibrium adsorption catalysts used for activity testing in this part were obtained from a different batches. It showed slightly higher in activity and slightly lower in selectivity. However, it was within 12% of reproducibility.