

CHAPTER V

CONCLUSION AND SUGGESTION

In situ decomposition of ammonium tetrathiomolybdate (ATM) and tetrabutylammonium thiomolybdate (TBATM) is a very effective method for the preparation of highly active MoS₂ catalyst. The thermal decomposition of thiosalt precursors to obtain MoS₂ involves elimination of alkylammonium cations to get MoS₃ and, after that, simultaneous reduction of Mo⁺⁶ to Mo⁺⁴ and sulfur elimination.

The *in situ* generated MoS₂ and Co/MoS₂ catalysts from ATM and TBATM precursors with and without added water were characterized by XRD, BET, EDX and SEM. For non-promoted MoS₂ catalysts, XRD patterns of all *in situ* generated MoS₂ showed poorly crystalline structure of MoS₂. The results of BET analysis are shown that *in situ* generated MoS₂ catalyst prepared from ATM+H₂O have much higher surface area (544 m²/g). The relative range of surface area as a function of precursors was: ATM+H₂O (544 m²/g) > TBATM (270 m²/g) > ATM (120 m²/g) > TBATM+H₂O (83 m²/g). EDX analysis reveals high C/Mo ratios (2.9 – 8.9) for all MoS₂ catalyst especially from ATM+H₂O. It might be due to formation of sulfocarbide phase. N₂ adsorption-desorption for all *in situ* generated MoS₂ catalysts present type IV isotherm with desorption curves characteristic of mesoporous materials. SEM micrographs of *in situ* generated MoS₂ catalyst prepared from ATM+H₂O are much more porous and their surface are rough while derived from ATM have flat and smooth surface with stack layer of MoS₂. *In situ* generated MoS₂ catalyst from TBATM have much cheese-like cavities morphology, observed is produced by the internal pressure generated by the vaporization of the organic alkyl groups during the decomposition steps of TBATM precursor under high pressure of hydrogen and high temperature. The water addition in runs of TBATM retards the formation of an organized porous system.

For the cobalt promoted with ATM and TBATM precursors. XRD patterns still exhibited poorly crystalline structure of MoS₂ together with the cobalt sulfide phase. XRD pattern of *in situ* generated MoS₂ catalyst from ATM+H₂O present very

weak in intensity of peaks of cobalt sulfide phase, suggesting that promoter atoms are well dispersed on the active phase. Co/Mo ratios of Co/MoS₂ catalyst were found to range between 0.1 and 0.36. High C/Mo ratios of 0.36 for Co/MoS₂ catalyst from ATM+H₂O, suggesting that cobalt sulfide are well dispersed on the active phase. Results obtained from BET measurements show that cobalt promoter lead to a decrease in surface area compared to the non-promoted MoS₂ catalysts. N₂ adsorption-desorption presents only a type I isotherms for *in situ* generated Co/MoS₂ catalysts from ATM+H₂O+Coacetate, while a type IV isotherms is already formed for *in situ* generated Co/MoS₂ catalyst from ATM and TBATM precursors. The morphology of *in situ* generated Co/MoS₂ catalyst show that, cobalt addition does not change markedly the morphology of the Co/MoS₂ catalysts compared with MoS₂ catalyst.

For the hydrodesulfurization of dibenzothiophene catalyzed by *in situ* generated MoS₂ from ammonium tetrathiomolybdate (ATM), it was found that hydrogen pressure, reaction time, DBT/Mo mole ratio affected the catalytic activity of HDS. The hydrodesulfurization of DBT is retarded by the presence of quinoline because nitrogen compound adsorb competitively with the reactant DBT on the active sites of MoS₂ catalyst. *In situ* generated MoS₂ catalyst from TBATM show higher HDS activity than formed from ATM, the presence of butyl group in TBATM precursor has an important effect on the surface area and total pore volume of MoS₂ catalysts, leads to a strong increase in HDS activity.

Cobalt and nickel addition enhanced HDS activity of both MoS₂ catalysts from ATM and TBATM precursors, Co/MoS₂ catalyst usually shows higher activity than Ni/MoS₂ catalyst for HDS of DBT.

When added water to the runs with ATM, the results showed a strong synergetic effect of water addition, while the runs of TBATM with added water, %conversion of DBT decreased. That might be due to the decreasing of surface area of *in situ* generated MoS₂ catalyst from TBATM+H₂O caused the decreasing in the active sites of catalyst.

The use of ATM and water together for *in situ* generation of MoS₂ catalyst can lead to 100 %conversion of HDS of 4,6-dimethyldibenzothiophene under 30 atm H₂ pressure at 350 °C in decalin solvent. Model reaction suggested that water addition led to a high surface area, highly active MoS₂ catalyst. Better MoS₂ catalyst with higher surface area (559 m²/g) obtained with the mole ratio of H₂O/ATM = 1200. Additionally, the results showed that the *in situ* generated MoS₂ catalysts from ATM+H₂O can reduce the sulfur contents of SRGO from 6100 ppm to 3250 ppm and from 310 ppm to 100 ppm in LCO.

Suggestion for the future work

Based on the above discussion and experimental results, the future work to improve the system should be focused on the following:

1. To study kinetic of the hydrodesulfurization of 4,6-dimethyldibenzothiophene catalyzed by *in situ* generated MoS₂ from ATM precursor with added water.
2. To study in two steps reaction. In the first step, the MoS₂ catalyst was *in situ* generated from decomposition of ammonium tetrahomolybdate (ATM) with added water to prepared highly surface area of MoS₂ catalyst. The hydrodesulfurization of sulfur model compounds or real oil feedstocks, as the second step.