



CHAPTER I

INTRODUCTION

1.1 Statement of problem

Air pollution by diesel exhaust gases in big cities has been one of the serious problems in the world. Environmental concerns are forcing dramatic changes in transportation fuel specifications. It is currently clear that transportation fuel quality will continue to be modified to improve both combustion quality and post-combustion gas clean-up performance. The exhaust gases from motor vehicles contain nitrogen and sulfur oxides, NO_x and SO_x . When these oxides expose to the atmospheric water, they transform to HNO_3 and H_2SO_4 , which cause the acid rain phenomenon. Moreover, sulfur is a well-known poison for catalytic converters [1].

Hydrocarbon fractions produced from petroleum industry are typically contaminated with sulfur in the form of organic sulfur compounds such as mercaptans, sulfides, thiophenes and dibenzothiophenes. These hydrocarbon fractions include diesel fuel and gasoline, including natural, straight run and cracked gasolines. Other sulfur-containing hydrocarbon fractions include the normally gaseous petroleum fraction as well as naphtha, kerosene, jet fuel, fuel oil, and the like. Typically oil fractions in the diesel boiling range will contain between 0.1 and 1.5 wt%S depending on the crude origin. This led the governments of numerous countries to adopt new regulations which aim to a drastic reduction of sulfur exhaust emissions.

In most country, the allowable limit on diesel sulfur will be restricted to 50 ppm within another 5 years [2, 3]. In the European Union, the maximum permissible sulfur content of diesel will be reduced from 50 ppm to 10 ppm in the year 2009 [4]. Now, in USA, the sulfur content of diesel fuel is down to 50 ppm and 15 ppm in Japan. In Thailand, the Ministry of Energy plans to further reduce sulfur in diesel to below 350 ppm.

Because of these regulatory actions, the need for more effective desulfurization methods is always present. The most common method of desulfurization of fuels is hydrodesulfurization, in which the fuel is reacted with hydrogen gas at elevated temperature and high pressure in the presence of a costly catalyst. Hydrodesulfurization has long been used to reduce the levels of sulfur in the product fractions and in general this has proved effective.

Hydrodesulfurization is routinely carried out in oil refineries using commercial catalyst, CoMo/Al₂O₃ which is prepared by coimpregnation of Mo salt on alumina support, followed by sulfidation with H₂/H₂S. Typically severe condition is needed (T = 300 - 650 °C, P = 30 - 170 atm). Due to their exceptional resistance to poisons, transition metal sulfides, mainly molybdenum and tungsten disulfide promoted with cobalt or nickel, are widely used in this process. Generally, molybdenum and tungsten sulfide catalysts are prepared from oxide precursors by sulfidation using either H₂/H₂S.

Preparation of catalysts with better catalytic activity and stability than commercial ones presents a great challenge for the refining industry and the search of new routes of preparation is an area of current interest.

1.2 The objectives of research

The objectives of thesis can be summarized as follows:

1. To synthesize and characterize tetrabutylammonium thiomolybdate (TBATM) precursor.
2. To characterize MoS₂ and Co/MoS₂ catalysts generated *in situ* from decomposition of ammonium tetrathiomolybdate (ATM) and tetrabutylammonium thiomolybdate (TBATM) precursor with and without cobalt promoter.
3. To study various effects on the hydrodesulfurization of dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) using *in situ* generated MoS₂ catalyst.

4. To study the hydrodesulfurization of real oil feedstock; straight run gas oil (6100 ppmS) and light cycle oil (310 ppmS) using *in situ* generated MoS₂ catalyst.

1.3 The scope of research

In the present work, ammonium tetrathiomolybdate (NH₄)₂MoS₄ and tetrabutylammonium thiomolybdate precursor [(CH₃CH₂CH₂CH₂)₄N]₂MoS₄ were used *in situ* to prepared active unsupported MoS₂ catalysts for hydrodesulfurization of a most refractory model compound of dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT). Hydrodesulfurization of real oil feedstocks, straight run gas oil (SRGO) of 6,100 ppmS and light cycle oil (LCO) of 310 ppmS were also investigated on the same catalyst precursors for comparison.