



CHAPTER I

INTRODUCTION

Arsenic occurs abundantly in nature, with an average concentration of 2.5 mg/kg in earth's crust and 2.5 $\mu\text{g}/\text{dm}^3$ in ocean water (Cox, 1989). Arsenic is not only present in inorganic materials such as water, rocks and soils, but also in organisms particularly in marine organisms and in crude petroleum (Irgolic et.al.,1991). Arsenic is usually found in petroleum, crude oil and shale oil. The concentration of arsenic in these hydrocarbon often exceed 20 ppm, with value typically ranging from 0.111-0.263 ppm for petroleum (Fish and Brinckman, 1983), from 20 to 80 ppm for full range shale oil derived from Colorado oil shale and from 20 to 1200 ppm for many coal tar distillates (Albertson, 1984). Arsenic in raw oil shale is usually associated with pyrolytic materials (Desborough et al., 1976). Unlike trace metal contaminants in petroleum, arsenic is distributed throughout the hydrocarbon boiling ranges. During retorting, it derives from many volatile compounds such as arsenic sulfide and arsine (Fox et al.,1977). Subsequent reaction with hydrocarbon leads to the formation of various types of arsenic compounds including: arsenate, phenylarsenic acid and neutral organic compounds such as trialkylarsine oxide (Weiss etal.,1981). Hence, the structures of arsenic in

petroleum are organometallic and inorganic compounds. Catalytic processes applied in petroleum industry are generally large-scale, continuous process operating without interruption for long intervals. This is made possible by employing suited catalyst and by adequate safeguarding against catalyst deactivation. One of the most practical problems in the catalytic process is presented by the loss of catalytic activity during reaction within a porous catalyst medium. Arsenic is generally considered to be one of the most potent poisons (Merryfield et al., 1984) and is a serious poison even presently at 50 ppb levels (Carr, 1992). It acts as a reforming and hydrotreating catalyst poison because of its affinity for the metals platinum, cobalt, nickel and the like (Goyal, 1988). Left in the feedstock, arsenic will deposit on active site or block pore mouth of upgrading catalysts causing permanent loss of catalyst activity (Burger et al., 1975). Also, arsenic deposits on high temperature naphtha cracker tube surfaces to cause coke build-up, reduced production and reduced product selectivity. Arsenic in petroleum is also considered to be hazardous waste products and poses serious disposal problems. In addition of causing processing difficulties, arsenic content limits the usefulness of petroleum even in unrefined state. (Even if the petroleum is employed directly as a fuel, since burning high-containing arsenic results in unacceptable pollution.)

There is an extremely wide variation in toxicity of arsenic and its organic and inorganic compounds.

North American government has developed quality criteria for allowable levels of inorganic and organic compounds in air and water (Legault et. al.,1993). They limit the present exposure of arsenic in air and drinking water are 0.5 mg/m^3 and 50 ppb, respectively. Arsenic in petroleum is set lower than 50 ppb to avoid any potential problem during transportation and upgrading (charr, 1992). To avoid the premature replacement of expensive catalyst and environmental reasons, it is necessary to reduce the arsenic in petroleum to low levels before use as a source of energy or further processing.

Recent economics and environmental reasons have resulted in raising to the development of arsenic removal. Three methods have been developed to remove arsenic from petroleum, namely thermal treatment, chemical treatment, and adsorption on inorganic material. The first method is used for removing of arsenic by heat treating. Following the heat treating step, some of arsenic compounds are converted to precipitate form. The converted arsenic compounds can be separated from feedstock by physical separation (Curtin, 1977). Chemical treatment uses oxidizing agent to convert a portion of arsenic to more easily extractable by water. Thereafter, the converted arsenic is dissolved and removed from feedstock by water (Delaney, 1988). Adsorption currently the most widely used method on an industrial scale (Oleck, 1987). It provides a process for removing arsenic by contacting feedstock with an adsorbent. Under suitable condition, arsenic will be contacted and adsorbed on adsorbent. In spite of the

development of powerful and very costly method, adsorption on inorganic material continues to be a simple, elegant, versatile and inexpensive method for arsenic removal (Charr, 1992). Adsorption method provides that the concentration of arsenic in petroleum remains at low level before utilizing (Debras, 1987).

Although several adsorption methods have been developed over the years, none of the existing methods of arsenic removal is ideal and universal (Nowack, 1991). In the past, most of them have only aimed to remove arsenic to low concentration as possibility (usually less than 50 ppb). Observation of the literatures show that almost of arsenic removal by adsorbent is prosperity in gas phases for high efficiency (Carr and Stahlfeld, 1985; Debras, 1987). On the other hand, the efficiency of arsenic removal in liquid phase is lower than gas phase. In addition, the removal of arsenic in liquid phase is encountering for problems of deterioration. One of the factors expected for the declining efficiency of arsenic removal concerns with different forms of arsenic in gas and liquid phase. The difference in extent of removal of arsenic compounds depends on the structure of the compounds (Carr et al., 1985)

Many researches have been studied the mechanism of arsenic depositing on adsorbent. However, the mechanism is not completely understood and many conflicting views have been reported (Nowack et al., 1986; Ng, 1991). This makes no indication to show that what forms of arsenic can be removed by adsorbent. It shows that each forms of arsenic displays different roles

in removing process. That makes uncertainly prediction in arsenic removal (Johnson et al., 1986; Nowack et al., 1991; Ng and Chang, 1991). Since the characterization of arsenic is considered to play major roles in arsenic removal. This research will investigate what forms of arsenic can be removed and compared the efficiency of arsenic removal at different forms of arsenic.

From the literature reviews, the nickel-molybdenum oxide adsorbent has been frequently used for removing arsenic in petroleum (Sullivan, 1979). A beneficial role of Ni-Mo/Al₂O₃ for arsenic removal in liquefied feedstock is dominance compared to the others (Oleck, 1986). Nickel oxides is recognized as an essential component of the active site for arsenic removal (Child, 1986). Although Ni-Mo/Al₂O₃ is suitable to remove arsenic, few studies indicated that Ni-Mo/Al₂O₃ can remove what forms of arsenic (Bebras, 1989). As the arsenic removal by Ni-Mo/Al₂O₃ was studied in one investigation and the major properties of Ni-Mo/Al₂O₃ was studied in another. It becomes difficulty to say that the discrepancy in arsenic removal depends on arsenical forms or adsorbents. The different results come from the different preparation of Ni-Mo/Al₂O₃ adsorbent. It is well know that catalyst activity and physical-chemical properties are very sensitive to any kinds of treatment. Therefore, it is important that adsorbent activities and physical-chemical properties are compared together. After some consideration, this attention focuses on the composition of the adsorbents comparison of the degree of arsenic removal.

The objectives of this reasearch are to prepare adsorbents with various nickel and/or molybdenum content and to determine the effect of nickel and/or molybdenum on arsenic removal. In the present study, fresh adsorbents are evaluated in a batch reactor to determine how the nickel and molybdenum affects the efficiency of arsenic removal. Toluene containing arsenic compounds is used as the feed model. Arsenic compounds, which are added in toluene, are organometallic and inorganic salt forms. The compositions of adsorbents are nickel oxide and molybdenum oxide on alumina supports. To prepare adsorbent by dry impregnation of alumina with active solution, ammoniummolybdate (VI) tetrahydrate and nickel nitrate solution are preferred. The product is characterized for arsenic concentration by Graphite Furnace Atomic Absorption Spectroscopy. The fresh and spent adsorbents are characterized by physical method, including surface area, pore volume and pore sizes distribution and X-ray Diffraction Spectroscopy (XRD).