

CHAPTER I

INTRODUCTION

Environmental concerns are forcing dramatic changes in motor fuel specifications. It is clear today that motor fuel quality will continue to be modified to improve both combustion quality and post-combustion gas clean-up performance. Petroleum oils used as feedstocks for diesel oils are middle distillates in the 180-400 °C boiling range. They include straight run gas oil, largely paraffinic, ranging from light gas oil to heavy gas oil that usually contain from 1 to 3 wt% sulfur. Various processes are used for upgrade heavier petroleum fractions to highly aromatic. The sulfur compounds present in the various oils are mostly aliphatic sulfides, benzothiophenes and dibenzothiophenes.

The need for cleaner burning fuels has resulted in a continuing worldwide effort to reduce the sulfur levels in gasoline and diesel fuels. The reduction of gasoline and diesel sulfur has been considered to be an important means for improving air quality because of the negative impact fuel sulfur has on the performance of automotive engine exhaust inhibitors and may irreversibly poison noble metal catalysts in the converter. Emissions from an inefficient or poisoned converter contain levels of non-combusted, non-methane hydrocarbons and oxides of nitrogen and carbon monoxide. Such emissions are catalyzed by sunlight to form ground level ozone, more commonly referred to as smog. With the concern over the impact of automotive air pollution continuing, it is clear that further efforts to reduce the sulfur levels in automotive fuels will be required

Sulfur content in diesel fuel is an environmental concern because upon combustion, sulfur is converted to SO_x during combustion, which not only contributes to acid rain, but also poisons the catalytic converter for exhaust emission treatment. The main sources of SO_2 emissions are the burning of fossil fuels (e.g., power plants and mobile sources) and the smelting of ores rich in sulfur. In the atmosphere, SO_2 can react with various oxidants (e.g., O_2 , O_3 , H_2O , NO_x , OH radicals) to form sulfate aerosol, either as sulfuric acid droplets, or as neutralized particles such as ammonium

sulfate, which play special role in atmospheric processes like acid rain and visibility degradation. Sulfur in petroleum products poisons catalytic converters, corrodes parts of internal combustion engines and refineries because of the formation of oxyacid of sulfur, and air pollution due to exhaust from diesel engines is a major concern to the public. The Ministry of Energy of Thailand has limited the sulfur level in diesel fuel to 0.035 %wt sulfur [ASTM D4294].

In the petroleum refining industry, hydrodesulfurization (HDS) is currently used for reducing the sulfur content of the liquid products. However, this process is not cheap for several reasons. One of them is the hydrogen pressure needed for kinetic and catalyst stability purposes. Another reason is related to benzothiophene or dibenzothiophene compounds that constitute very refractory molecules in the process, resulting in significant difficulty in achieving the very low sulfur content presently required in the liquid fuel. The effectiveness of the HDS process depends on the type of sulfur compound. The complete removal of sulfur present in petroleum as sulfides, disulfide and mercaptans is relatively easy and an inexpensive process. However, benzothiophenes and dibenzothiophenes (DBTs) are difficult to remove by this process. Most of sulfur contamination in petroleum can be traced to the dibenzothiophene derivatives. In order to remove these compounds by HDS, it would require more hydrogen capacity and the maintenance of high temperature and pressure for longer time periods. This would increase operating costs and enhance the likelihood that saturation of olefins and aromatics will occur resulting in a lower-grade fuel and additional processing steps. Thus, it is likely that HDS processing has reached a stage where increasing temperature and pressure are just not enough to remove the residual sulfur without affecting the octane number. This process also produces increased volumes of hydrogen sulfide. Although HDS processes have dominated desulfurization of petroleum in the past, their cost and the requirements of strict fuel specifications combine to motivate the development of innovative process technology. All of these methods incur a cost penalty and this stimulated our interest in alternative form of desulfurization.

Oxidative desulfurization (ODS) is considered to be one of the promising new methods for deep desulfurization of fuel oil. Compare with the conventional catalytic hydrodesulfurization (HDS), ODS can be carried out under very mild condition: at room temperature and under atmospheric pressure. The divalent sulfur of dibenzothiophene (DBTs) can be oxidized by the electrophilic addition reaction of oxygen atom to the hexavalent sulfur of sulfones. The chemical and physical properties of sulfones are significantly different from those of hydrocarbon fuel oil. Therefore, they can easily removed by such separation operations as distillation, solvent extraction, adsorption, and decomposition. Many different type of oxidants have been used, including $\text{HNO}_3/\text{CH}_3\text{COOH}$, NO/NO_2 , NO_2 , HNO_3 , $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$, *t*-BuOOH and O_3 . Use of nitrogen oxides as oxidizing agent can have the double effect of oxidizing the sulfur compounds present in the oil: nitroaromatics are thought to have high cetane number. However, reaction selective, safety and cost are the important concerns for the selection of oxidant, catalyst and operating conditions for ODS processing. The advantage of the ODS process that expensive hydrogen is not used. Another feature of ODS is that the refractory sulfur compounds in HDS are easily converted by oxidation.

Polyoxometalates (POMs), a class of molecularly defined inorganic metal oxide clusters, which combine strong acidity with high redox and acid-base properties, are well known to be very effective catalysts for both acid-catalyzed and oxidation [1]. POMs with Keggin structure are composed of a central tetrahedral (XO_4^{n-}) surrounded by 12 linked octahedra containing the addenda atom ($\text{M}_{12}\text{O}_{36}$) (Figure1). The overall charge of the central tetrahedral is delocalized over the entire structure. Although other metals could be used as central atom, phosphorus leads to the more stable anions and is most of the time present in heteropolycompounds used as catalysts. The catalytic function of the Keggin type, the kinds of metal substituted polyoxometalate structures has attracted much attention particularly because these compounds provide a good basis for the molecular design and high capabilities in practical uses. There are several large-scale industrial processes that use heteropolyoxometalates as oxidation and acid catalysts both in the solid state and in solution. Heteropoly catalysts are promising green catalysts since most of them are environment friendly.

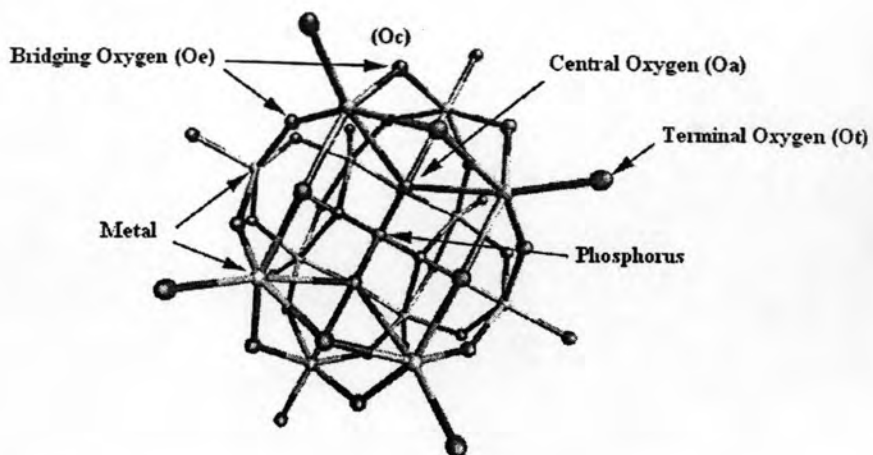


Figure 1. Primary structure of the polyoxometalate (Keggin structure).

1.2 The objectives of thesis

The objectives of thesis can be summarized as follows:

1. To synthesize and characterize polyoxometalate catalysts.
2. To study catalytic performance of the synthesized catalysts for the oxidation of model sulfur compounds (benzothiophene, dibenzothiophene and 4,6-dimethyldibenzothiophene).
3. To utilize the catalytic system for oxidation of diesel fuels.