

## Chapter 14

# Polyoxometalates–Based Nanocatalysts for Production of Sulfur–Free Diesel

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### ABSTRACT

*In the last decade, polyoxometalates have been demonstrated to be efficient catalysts for the activation of oxidants in desulfurization processes. Successful results on desulfurization using polyoxometalates and hydrogen peroxide to desulfurize model oils and liquid fuels were reported and can be found in the literature. The desulfurization is an actual subject with notable interest for refineries and fuel cost, and consequently it is important to focus the scientific community to work in desulfurization technology in order to develop catalytic systems based on polyoxometalates capable to be reused, stable, efficient and selective. Therefore, the main goal is the design of heterogeneous polyoxometalate based catalysts. This chapter pretends to inform the research society about the scientific directions that have been taken using heterogeneous polyoxometalate catalysts in oxidative desulfurization of simulated and real liquid fuels. In addition, future perspectives are proposed to cover the actual needs of this area.*

### INTRODUCTION

The specifications that govern transportation fuels have become increasingly stringent with respect to sulfur content, over the years. Consequently, the removal of sulfur from oil is consequently one of the central requirements in most refineries and the price of a crude oil is influenced by its sulfur content. The refining cost (financial and environmental) increases as heavier and more sulfur-rich crude oils are being processed. Sulfur is the most abundant element in petroleum after carbon and hydrogen. The average

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sulfur content varies from 0.03 to 7.89% (in mass) in crude oil.(Soleimani, Bassi, & Margaritis, 2007) Organic sulfur molecules such as thiols, sulfides, and thiophenic compounds represent the main source of sulfur found in crude oil (Figure 1). Desulfurization of compounds that contain aliphatic sulfur, i.e. thiols and sulfides, is easier than desulfurization of compounds that contain aromatic sulfur, i.e. thiophenics.

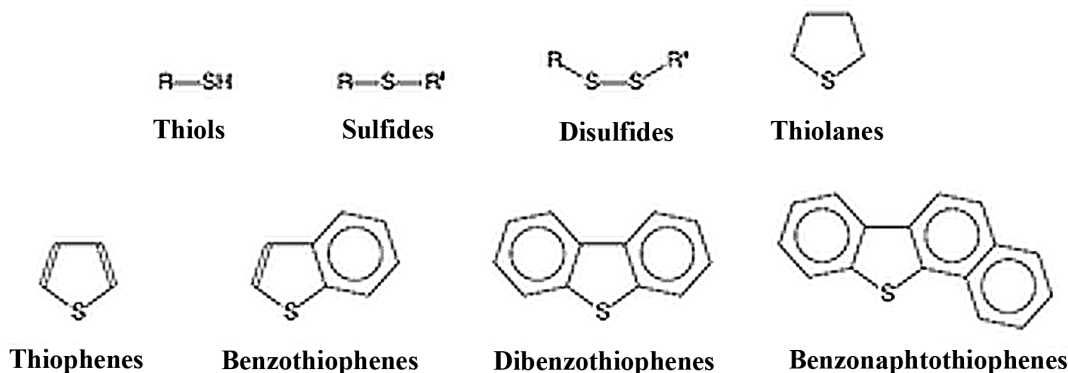
The actual desulfurization process applied in petroleum refining for treating sulfur content in transportation fuel, is the hydrodesulfurization (HDS), which is a simple and proven process for the refiners. The HDS technology has been adjusted to meet the tight specifications of the current limit imposed by government directives for liquid fuel transportation of 10 ppm.(Lissner, de Souza, Ferrera, & Dupont, 2009; Y. Liu et al., 2013) However this requirement has forced the HDS units to operate at extreme severe conditions (high temperature, pressure and consume of large amounts of hydrogen) and/or with higher catalyst volumes, do not only affect the economic viability of the process but most importantly the fuel specifications are affected.

The strict sulfur directives associated to the high cost of the actual HDS process requires the development of alternative or complementary desulfurization technologies, mainly for the removal of the aromatic sulfur-compounds which are the most difficult to eliminate from diesel fuels.

The oxidative desulfurization (ODS) is considered one of the most promising alternative or supplementary process, offering several advantages over HDS, such as mild reaction conditions (operating under atmospheric pressure), high selectivity and economic viability. In the ODS process the sulfur-containing compounds are oxidized to the corresponding sulfoxides and/or sulfones which are more easily removed from fuels by extraction, adsorption or other appropriate techniques.(Lü, Ren, Wang, et al., 2013; Nie, Dong, Bai, Dong, & Zhang, 2013)

Early-transition metal oxygen anion clusters, also known as polyoxometalates (POMs), are a class of compounds with high interest for application in different areas such as, medicine,(Rhule, Hill, Judd, & Schinazi, 1998) materials science,(Coronado & Gómez-García, 1998) photochemistry,(Katsoulis, 1998; Yamase, 1998) biology(Yamase, 2005) and catalysis(Mizuno & Misono, 1998; Proust, Thouvenot, & Gouzerh, 2008). In particular, POMs have been extensively used as catalysts due to their unusual versatility and compatibility with environmental friendly conditions and operations, being designated by “green catalysts”.(Hill & Prosser-McCarthy, 1995; R. Wang, Zhang, & Zhao, 2010) The first POMs applied as catalysts in ODS systems were the tetrabutylammonium salts of  $[W_6O_{19}]^{2-}$ ,  $[V(VW_{11})O_{40}]^{4-}$ ,  $[PVW_{11}O_{40}]^{4-}$ , and  $[PV_2Mo_{10}O_{40}]^{4-}$ .(Komintarachat & Trakarnpruk, 2006) Since 2011 the use of POMs

*Figure 1. Schematic representation of some sulfur-compounds present in crude oil.*



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