# Chapter 6
# Advances in Nanotechnology Transition Metal Catalysts in Oxidative Desulfurization (ODS) Processes:
## Nanotechnology Applied to ODS Processing

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## ABSTRACT

*Organosulfur compounds show a negative environmental impact because of SOx emissions by combustion of fuel oils. As a consequence, removal of sulfur is becoming a worldwide challenge. The hydrodesulfurization (HDS) process achieves limited performances in the case of refractory S-containing aromatic compounds, such as thiophene and substituted benzothiophenes (BTs), which require highly energy-demanding conditions (high temperature and pressure conditions). Oxidative desulfurization (ODS) is considered the most promising alternative to HDS. During ODS treatment, the organosulfur compounds are oxidized to corresponding sulfoxides and sulfones, which can be successively removed by extraction with polar solvents. Different stoichiometric oxidants have been used in the ODS processes with a different degree of efficacy and environmental impact. The design and development of catalytic procedures can increase the ODS energy efficiency as well as make it more economical and environmentally acceptable. Here we describe the advances in nanostructured organometallic catalysis and biotechology applied to ODS treatment.*

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## INTRODUCTION

The removal of sulfur compounds in petroleum and fuels represents an important topic for the protection of the health of our planet, (Oliveira et al., 2013; Teixeira, Oliveira, Cristofani, & Moura, 2013). As a consequence of the combustion process, sulfur compounds are oxidized to corresponding sulfur oxides and acids that significantly influence the composition and stability of the atmospheric ozone layer, as well as the formation of acid rain, (De Souza, Guimaraes, Guerreiro, & Oliveira, 2009). These environmental risks prompted the U.S. Environmental Protection Agency (EPA) to issue a maximum sulfur content (15 ppm) in diesel fuel, a limit that was further reduced in the Euro V standard protocol (10 ppm). Thus the development of new technologies for deep sulfur removal has become an enormous challenge for production of clean fuels, (Song, 2003). The conventional procedure for the removal of sulfur contaminants in fuel is hydrodesulfurization (HDS), (Satterfeld, 1991; Speight, 1998). The HDS process consists in the hydrogenolysis reaction at elevated temperatures (ranging from 300 to 400 °C) and elevated pressures (10-130 atm) in the presence of catalysts, which are typically based on alumina or silica supports impregnated with different metal species (such as cobalt, molybdenum and nickel), (Schuit & Gates, 1973). The more challenging problems of HDS stem from the recalcitrant nature of aromatic sulfur compounds, such as benzothiophene (BT), dibenzothiophene (DBT) and other methyl substituted derivatives, which can irreversibly plug the active sites of catalyst, influencing the kinetic and the flow distribution in the reactor, (Babich & Moulijin, 2003). The oxidative desulfurization (ODS) is a promising alternative to HDS for the production of ultra low sulfur fuels, (Zannikos, Lois, & Stournas, 1995). In the ODS process, the stable and difficult-to-reduce DBT derivatives are oxidized to corresponding sulfones and sulfoxide under low temperature and pressure conditions. These polar derivatives are successively separated from the fuel by either extraction or adsorption units, (Campos-Martin, Capel-Sanchez, Perez-Presas, & Fierro, 2010). The ODS process is complementary to HDS, since some sulfur compounds, such as disulfides, are easy to be reduced but oxidize slowly. For this reason, ODS process is mainly applied for the treatment of fuel with low content of sulfur contaminants (500 ppm), already depleted of oxidation stable species, (Gatan, Barger, Gembicki, Cavanna, & Molinari, 2004). The oxidation of organic sulfur compounds is usually accomplished by the use of stoichiometric oxidants, such as potassium permanganate ($KMnO_4$), (Gokel, Gerdes, & Dishong, 1980) sodium bromate ($NaBrO_3$), (Shaabani, Behnam, & Rezayan, 2009) different carboxylic peracids, (Kubota & Takeuchi, 2004) sulfonic peracids (Kluege, Schulz, & Liebsch, 1996) and many other oxidants, (Shefer & Rozen, 2010; Hudlicky, 1990). On the other hand, increasing environmental concerns raised the interest to develop benign, selective and economical procedures, based on catalytic methods. Exhibiting both homogeneous and heterogeneous catalytic properties, nanocatalysts allow for rapid and selective chemical transformations, taking advantages of excellent conversion of substrate, product yield and easiness of catalyst separation and recovery (Zhang, Xu, & Wang, 2014). The high performance of these systems is related to the possibility of design nanomaterials with specific and carefully tuned catalytic properties by specific nanosized methodologies, including metal-metal oxide, metal-metal, metal-non-oxide and metal alone supporting procedures (Polshettiwar & Varma 2010). Nanosized materials show additional unique properties compared to macroscale (Campelo et al., 2009) which are associated at the high surface to volume ratio (S/V) of the catalytically active material (Teunissen, Bol, & Geus, 1999). Nanocatalysts, with dimensions of less than 100 nanometers (100 nm), have been used in ODS processes in the last years to activate primary oxidants, such as hydrogen peroxide ($H_2O_2$), alkylperoxides and peracids. In the following sections, a large panel of well recognized nanocatalysts for ODS will be described,