



# Highly reactive magnetite covered with islands of carbon: Oxidation of N and S-containing compounds in a biphasic system

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## ABSTRACT

In this work a series of magnetite were prepared by impregnating of natural goethite (limonite) with glycerol before thermal treatment under N<sub>2</sub> flow at 300, 400 and 500 °C. The formation of carbon spots (island) over magnetite was found. The magnetite was found to be the main phase after treatment at 400 and 500 °C with high content of Fe<sup>2+</sup>, which is the active specie in a Fenton like system. Furthermore, iron oxide particles with magnetic and amphiphilic properties were formed, which are interesting for using as a catalyst in refineries. All materials presented high catalytic activities for oxidation of quinoline and dibenzothiophene in a biphasic reaction system (water/toluene).

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## 1. Introduction

Sulfur compounds in fuel oils are known to have a negative impact onto the environment because of SO<sub>x</sub> emissions from their combustion exhausts. Consequently, removal of sulfur (present in organic sulfur compounds like thiophenes, benzothiophenes (DBT) and its derivatives, thiois, mercaptans and others), is becoming a worldwide challenge due to more stringent regulations and in order to prevent exhaust catalyst deactivation [1–3]. The oxidative desulfurization process (ODS) has received much attention for deep desulfurization of middle distillates because of two main advantages relative to the hydrodesulfurization (HDS) process [4]. First, the major advantage of the ODS over HDS process is that it can be carried out in the liquid phase and under very mild conditions. Second, the most refractory sulfur-containing compounds to the HDS process [e.g., dibenzothiophene (DBT) and its alkylated derivatives] show high reactivity toward the oxidation by ODS method. DBT can be oxidized by the electrophilic addition reaction to sulfones and sulfoxide. The chemical and physical properties of sulphones are significantly different from those of hydrocarbon in fuel oil. Therefore, they can easily be removed by such separation operations as distillation, solvent extraction [5,6]. The ODS process can be

complementary to the HDS process because is difficult or very costly to use the existing HDS technology to reduce the sulfur in the fuels to less than 50 mg L<sup>-1</sup> [7].

In ODS process is important to evaluate the effect of the presence of other compounds in the oil fraction. In addition, it has been observed that the N- and S-containing compounds coexist in many kinds of fuel oil [8]. Denitrogenation is considerably more difficult than desulfurization because the organonitrogen compounds are much less reactive than the organosulfur compounds [9,10]. As a part of this work we evaluate the effect of the N-containing compounds on the oxidative desulfurization reactions, i.e., oxidation of dibenzothiophene in the presence of quinoline.

Several types of oxidants and different catalysts have been examined for the ODS process. Oxidants used include hydrogen peroxide [11–13], organic hydroperoxides (e.g., tertbutyl hydroperoxide) [14,15], air [16], and other that including the combination of H<sub>2</sub>O<sub>2</sub> with organic acid [17,18]. Most of the reported ODS systems involve use of the oil-insoluble oxidants, H<sub>2</sub>O<sub>2</sub> or peroxides, which results in a biphasic oil–aqueous solution system. Biphasic systems limit the mass transfer through the biphasic interfaces in the oxidation process, which leads to decrease the oxidation rate.

Iron oxides have shown potential application in ODS system, particularly after surface modifications to generate active species [7,19]. Limonite, an iron oxide source that is a waste from nickel ore, is a mixture of minerals that displays the goethite phase (α-FeOOH – 75%) as the main constituent that presents interesting catalytic properties. However, this material remains preferably in hydrophilic phase causing a low reaction rate and low conversions

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