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



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1. Introduction

Sulfur compounds in fuel oils are known to have a negative impact onto the environment because of SO_x 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

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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_2 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 Fe²⁺, 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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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^{-1} [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_2O_2 with organic acid [17,18]. Most of the reported ODS systems involve use of the oil-insoluble oxidants, H_2O_2 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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Fig. 1. Schematic representation on the limonite-glycerol composites (a) and formation of the carbon islands and regions containing active Fe²⁺ on the catalyst (b).

[20]. For this reason, limonite and other material based on iron oxide need to be modified to generate hydrophobic regions on the catalyst surface. In this work, the limonite was treated with a glycerol to create islands of carbon on the surface of iron oxide in order to generate amphiphilic properties and also create regions rich in Fe^{2+} [21].

In this context, the objective in the present study was to explore a novel ODS material, which is more energy efficient, present lower cost and it is environment friendly. This ODS method combines a catalytic oxidation step in the presence of H_2O_2 at mild conditions and an extraction liquid step using methanol solution. The potential advantages of this novel ODS method are: (i) the process attempt to use green chemical as an oxidant, which are readily available, low cost, and suitable for desulfurization applications; (ii) natural iron oxide (Fenton active phase – Fe^{2+} and a hydrophobic region) impregnated with island carbon (hydrophobic regions), forming an amphiphilic catalyst to act in a biphasic oil–aqueous-solution system.

2. Experimental

2.1. Catalyst preparation and characterization

All chemicals were high purity grade and were used as purchased. Limonite ore samples (45–46 wt% of Fe 75% of which are as goethite form), from mines located in Goias State (Central Brazil), were ground and sieved below 100 mesh (Tyler series), dried for 1 h at 120 °C. This material was impregnated with a glycerol–acetone solution (10%, v/v), in proportion of iron oxide 5 g to 100 mL of glycerol solution. The material was maintained under stirring at 80 °C until total evaporation of the solvent. The limonite–glycerol composite was thermal treated under N₂ atmosphere at three temperatures: 300 °C (Gli 300), 400 °C (Gli 400) and 500 °C (Gli 500), rate 10 °C min⁻¹, with flow of 50 mL min⁻¹. The scheme showed in Fig. 1 represent all steps used for the treatment to the formation of the amphiphilic materials.

2.2. Catalyst characterization

Mössbauer spectroscopy experiments were carried out at room temperature in a spectrometer model MA250 with a 57Co/Rh source, using α -Fe foil as reference. The powder XRD data were obtained in a Rigaku model Geigerflex using Co Kα radiation scanning from 10° to 80° 2 θ at a scan rate of 48 min⁻¹. Natural limonite and the sample with treatment were analyzed by FTIR using an Excalibur FTS 3000 from Bio Rad. Samples were pressed into 7 mm discs using 1-5% mixture of the sample and spectroscopic grade KBr. The limonite and Gli materials were observed by a JEOL JSM 6400 scanning electron microscopy. Moreover, an EDS probe was used to determining their elemental compositions. TPR experiments were performed in a CHEMBET 3000 using 40 mg sample and a flow rate of 80 mLmin⁻¹ of a mixture of H₂ (5%) and N₂ with heating rate of 10 °C min⁻¹ from room temperature to 1000 °C. Thermogravimetric analysis TGA (Shimadzu DTG-60AH) was made in the following conditions: N₂ atmosphere with a heating rate of 10 °C min⁻¹, gas flow of 30 mL min⁻¹ and initial mass about 3.0 mg. The surface area was determined with the BET method using N₂ adsorption/desorption at 77 K in an Autosorb 1 from Quantachrome Instruments.

2.3. Catalytic tests

The oxidative reactions were performed were magnetically stirred at 25 °C (\pm 2 °C). The catalytic activity of the materials was tested on the oxidation of quinoline (50 mg L⁻¹) using toluene as a solvent. The catalytic tests at pH 4.0 (natural pH of the H₂O₂//HCOOH solution) were carried out with a total volume of 10 mL (9.9 mL of quinoline solution and 0.1 mL of the equimolar solution H₂O₂//HCOOH) and 10 mg of catalyst. Quinoline removal from toluene phase was monitored by GC–MS. Polar compounds was monitored by electrospray ESI-MS (Agilent-1100), aiming to identify intermediates formed during this reaction. ESI-MS/MS experiments in the positive ion mode were also performed. The reaction samples were analyzed by infusion into the ESI source with



Fig. 2. The quinoline and DBT chemical structures.

a syringe pump at a flow rate of 5 μ Lmin⁻¹. The spectral data so obtained were averaged from 50 scans of 0.2 s each. Typical ESI-MS conditions were as follows: heated capillary temperature, 150 °C; dry gas (N₂) at a flow rate of 5 Lmin⁻¹; spray voltage, 4 kV; capillary voltage, 25 V; tube lens offset voltage, 25 V.

The catalytic properties of the amphiphilic material were tested via oxidation of dibenzotiophene (DBT), a model compound of sulfur contaminant from petroleum. In a typical run, 9.9 mL of a DBT solution (50 mg L⁻¹, in toluene), 10 mg of the catalyst and 0.1 mL of equimolar mixture H₂O₂//HCOOH as oxidant were added in the reactor. The oil phase was analyzed by GC-QP 2010 equipped with a HP-5 capillary column (30 m × 0.25 mm × 0.32 µm film thickness) and MS detector QP 2010 Plus.

It was also tested the catalytic capability of simultaneous oxidation of quinoline and DBT. The mixture contained $100 \,\text{mg}\,\text{L}^{-1}$ of quinoline and $50 \,\text{mg}\,\text{L}^{-1}$ of DBT in toluene was used. A selfextracting ability of the biphasic system was assessed with a solution methanol and assessed by ESI-MS. Fig. 2 presents the quinoline and DBT chemical structure.

3. Results and discussion

3.1. Catalyst characteristics

FTIR spectra of all materials are shown in Fig. 3. The FTIR spectrum of reference sample natural limonite corresponds to α -FeOOH. The resulting Fe—O and O—H bond lengths of the surface are once more different than those of the bulk [22]. The IR bands at 3442 and 3186 cm⁻¹ correspond to the stretching vibrations of adsorbed H₂O molecules and structural OH groups, respectively. Intensive bands at 900 and 793 cm⁻¹ are assigned to Fe—O—H bending



Fig. 3. FTIR spectra of samples natural limonite and Gli 300, Gli 400 and Gli 500, recorded at 20 $^\circ\text{C}.$



Fig. 4. TGA profiles for samples of natural limonite and Gli 300, Gli 400 and Gli 500, obtained under N_2 atmosphere.

vibrations, while the bands at lower wave numbers correspond to Fe–O and Fe–O–H stretching vibrations or lattice vibration bands [23].

The FTIR spectra of Gli 300, Gli 400 and Gli 500 materials showed two main absorption peaks in the range of $370-800 \text{ cm}^{-1}$, which are characteristic peaks of magnetite [24]. For Fe₃O₄ phase, two major bands at 590 and 408 cm⁻¹ are ascribed to Fe–O stretching modes of tetrahedral and octahedral sites in magnetite, respectively [25]. Signals related to vibration of OH groups of bulk are no longer present in the material after thermal treatment during the dehydration and reduction of goethite to magnetite. The natural and synthetic limonite samples were analyzed by thermogravimetric analysis (TGA). The TGA profile of the samples are shown in Fig. 4.

A total mass loss of about 12.9%, 8.2%, 4.6% and 2.8% was observed for natural limonite, Gli 300, Gli 400 and Gli 500, respectively, and this loss is predominantly in the temperature below 300 °C. The TGA profile shows at low temperature very small weight losses (in the temperature below 130 °C), since the thermoprocesses only comprise the removal of physically adsorbed water on the surface of materials. The loss of mass in temperature above 300 °C is related to structural loss of water due to loss of hydroxyl groups of goethite. Decrease in mass with the thermal treatment (300–500 °C) is related with conversion of goethite into magnetite phase (as shown in XRD analysis, Fig. 6) due to loss of the structural OH. The reduction capability of the samples were analyzed by TPR. The reduction profiles of the materials are shown in Fig. 5.

All TPR profiles were similar due to the fact that all samples presents similar composition and goethite (major constituent of limonite) is transformed into hematite by heating during TPR measurements. A sharp peak centered at approximately 425 °C was observed. A second H₂ consumption peak, centered at 750 °C was also observed. The first consumption peak accounts for the reduction of Fe₂O₃ (hematite) to Fe₃O₄ (magnetite). The second H₂ consumption peak is related to the reduction of magnetite to wustite (FeO) and metallic iron (Fe⁰). The samples thermal treatment leads to the decrease of the amount of hydrogen consumed, observed from the area under the peak. This fact is due to the reduction of Fe³⁺ to magnetite. A stead area decrease of the peak at 425 °C is observed with increase of temperature of treatment and it is related to Fe²⁺ sample enrichment. This process was observed previously for other iron oxide materials [13,18,26].

In order to identify the crystalline phases the materials were characterized by X-ray diffraction. The XRD patterns of all samples are shown in Fig. 6.



Fig. 5. TPR profiles for natural limonite, Gli 300, Gli 400 and Gli 500; heating rate 10 °C min⁻¹, under flow rate of 20 mL min⁻¹ of 5% H₂ in N₂.

XRD patterns of natural limonite sample (Nat Lim) confirmed the presence of α -FeOOH as main crystalline phase (JCPDS). The XRD pattern of Gli 300 material in Fig. 6 confirms the formation of mixture of iron oxide including a reduced iron oxide phase (magnetite–Fe₃O₄), showing that the deposition of carbon on the material surface also modifies the structure of the iron oxide. Gli 400 and Gli 500 presented magnetite as main phase. From here on we focused in natural limonite and Gli 400 materials due to the latter sample presented high activity in preliminary catalytic tests and the former was used for comparison.

In order to obtain information about the structural properties Mössbauer spectra of the samples were recorded (Fig. 7). From XRD analyses three phases are expected in the samples: α -FeOOH, Fe₃O₄, and α -Fe₂O₃.

Mössbauer spectra were obtained at 298 K for both materials. Natural limonite presents a central doublet due to the small particle size, notwithstanding the Mössbauer spectrum recorded at 77 K showed a sextet with magnetic ordered. The limonite



Fig. 6. XRD patterns of obtained powder samples, recorded at $20 \degree C$ (Gt = α -FeOOH, Mt = Fe₃O₄, and Hm = α -Fe₂O₃) Cu K α .



Fig. 7. Transmission Mössbauer spectra of natural limonite and Gli 400 powder measured at 298 K.

spectrum is fitted by two magnetically split subspectra, S₁ and S₂. The super-paramagnetic behavior of goethites has been attributed to the reduction of the magnetic coupling between the crystallites and the high concentration of vacant sites [27]. From the hyper-fine parameters of the sextet, obtained in fitting, 66% of iron is present as α -FeOOH ($B_{\rm hf}$ = 37.8 T). The remaining doublet can be assigned to dispersed superparamagnetic Fe³⁺. The Gli 400 material shows a Mössbauer spectrum characteristic for magnetite, Fe₃O₄, with a typical sextet observed for magnetic iron oxide presenting tetrahedral [Fe³⁺]^{tetra} and octahedral [Fe³⁺, Fe²⁺]^{octa} sites at 298 K.

The materials were also analyzed by SEM–EDS (Fig. 8). The natural limonite showed flat crystal faces and Gli 400 showed a different texture, with carbon island on the surface.

Elemental analysis of the materials revealing that the region in (a) likely composed of Fe and O are the dominant elements detected on the surface of the natural limonite in the proportions corresponding to FeOOH phase. However, the Gli 400 EDS (Fig. 8d) reveals that C is added to the surface of iron oxide after of impregnation with glycerol and thermal treatment. This elemental analysis showed the presence of a significant amount of C (approximately 49%), which generated a partial hydrophobic properties to Gli 400 catalyst [28].

3.2. Catalytic tests

The catalytic activity of the natural limonite and modified material were evaluated with respect to decomposition of hydrogen peroxide with the results presented in Fig. 9.

The most active catalyst for hydrogen peroxide decomposition is thermal treated material. This effect may be due to the fact that the surface reactivity of the oxides depended on the presence of reduced iron on the material surface, such as Fe²⁺. Firstly, Fe²⁺ plays an important role for the initiation of the Fenton reaction, according to the classical Haber–Weiss mechanism and therefore the enhancement of the rate of •OH production. As iron(II) presents a rate constant for hydrogen peroxide decomposition of $k_{Fo^{2+}} = 76 \text{ mol } \text{L}^{-1} \text{S}^{-1}$ which is faster than the rate constant



(c)

Fig. 8. SEM images for natural limonite and Gli 400 (a and c) and EDS analyses (b and d).

observed for iron(III) species $k_{\text{Fe}^{3+}} = 0.01 \text{ mol } L^{-1} \text{ S}^{-1}$ [29]. In a heterogeneous Fenton type reaction, a series of reactions occurs on the material surface. If only Fe^{3+} phase is present, Fe^{2+} is slowly generated by the reduction reactions as shown in Eqs. (2)-(4), initiating OH radical generation as shown in Eq. (1). In the case of

mixed Fe²⁺-Fe³⁺ species present in the material, reactions involving both Fe²⁺ and Fe³⁺ occur. Therefore, the presence of iron(II) in the material enhances the production rate of HO[•] [30]:

$$Fe_{surface}^{2+} + H_2O_2 \rightarrow Fe_{surface}^{3+} + HO^- + HO^{\bullet}$$
(1)

Fig. 9. Rate of hydrogen peroxide decomposition (a) and organic model compound oxidation (b) using iron oxide as catalyst: natural limonite and thermal treated materials. Experimental conditions: $T = 25 \circ C$; 30 mg of catalyst; 3.0 mL H₂O₂ 50%; 5.0 mL H₂O (a) and $T = 25 \circ C$; 10 mg of catalyst; 0.1 mL H₂O₂ 50%; 9.9 mL methylene blue 50 mg L⁻¹.

Fig. 10. Chemical structures of dibenzothiophene and its oxidation derivatives dibenzothiophene sulfoxide (DBTO) and dibenzothiophene sulfone (DBTO₂).

$$Fe_{surface}^{3+} + H_2O_2 \rightarrow Fe_{surface}^{3+}(H_2O_2)$$
(2)

 $Fe_{surface}^{3+}(H_2O_2) \rightarrow Fe_{surface}^{2+}(O_2H) + H_2O$ (3)

$$Fe_{surface}^{2+}(O_2H) \rightarrow Fe_{surface}^{2+} + HOO^{\bullet}$$
 (4)

For Gli 400 material, after 20 min of reaction, about 11.9 mL of O_2 were formed while the natural limonite formed only 1.5 mL. Gli 300 (6.5 mL of O_2) and Gli 500 (8.0 mL of O_2) are much less active than Gli 400, taking into consideration the activity of Gli 400 catalyst. Furthermore, the materials were evaluated in the oxidation of methylene blue, used as model molecule. According to the data presented in Fig. 9b, the material treated at 400 °C showed the highest rates of oxidation due to the presence of reduced iron sites combined of the accessible area of the material surface. The reduction at 500 °C compresses the material and make the process of diffusion at the interface of the catalytic material more difficult. So the Gli 400 material was select for the next catalytic tests.

Oxidation of sulfur atom in liquid phase followed by extraction of oxidized species can lead to desulfurization of diesel fuels. DBT oxidation mainly after reaction with Gli 400 catalyst generated DBTO (dibenzothiophene sulfoxide) and DBTO₂ (dibenzothiophene sulfore) as oxidation products (Fig. 10). The oxidation of the sulfur compounds in the toluene medium with Gli 400 catalyst was first carried without quinoline in a preliminary experiment aiming at identifying the reaction products. Fig. 11 shows the kinetics of DBT oxidation by the Gli $400//H_2O_2$ system.

The catalytic test for the oxidation of dibenzothiophene–DBT (a model molecule for fuel contaminant) was carried out in toluene and using the natural limonite and Gli 400 as a catalyst, the later showed high catalytic activity. The Gli 400 presented higher conversion (97%) after 180 min of reaction time (treatment with natural limonite removed about 45% of DBT after 180 min of reaction). This result clearly shows that the Fe²⁺ species (formed after

Fig. 11. Dibenzothiophene oxidesulfurization over Gli 400. Experimental conditions: $[H_2O_2 = 0.088 \text{ mol } L^{-1}]$; [catalyst]: $1 \text{ mg m} L^{-1}$; [DBT in toluene]: $50 \text{ mg} L^{-1}$.

thermal treatment with glycerol) are playing an important role in the catalyst activity. This catalyst, that was very active removing almost 100% of the DBT, has a great potential to be used in the removal S-compounds from fuel by an oxidative process, leading to more polar compounds as DBTO and DBTO₂ that can be removed from fuel by partition process [31].

Both nitrogen-containing and sulfur-containing compounds coexist in fossil fuels. Therefore it is essential to investigate the oxidation of sulfur-containing compounds in the presence of nitrogen-containing ones. It is known that nitrogen-containing compounds have a negative effect in the oxidation of sulfurcontaining compounds [32]. The authors attributed the lower activities to the poisoning of the active sites by nitrogen-containing compounds. On the other hand, Ishihara et al. [33] reported that nitrogen-containing compounds could be oxidized in the ODS oxidation system. This result suggests that the decrease in ODS activity can be related to the competition of the parallel oxidation of nitrogen-containing compounds. To clarify the effects of nitrogencontaining compounds in the DBT oxidation it was investigated the behavior of the oxidation process using both model compounds of nitrogen and sulfur containing molecules. The system used was quinoline/DBT//H₂O₂. Fig. 12 shows the DBT conversion in the presence of quinoline.

Fig. 12. DBT conversion with reaction time in the oxidation over Gli 400 catalyst in the presence of quinoline. Experimental conditions: [H₂O₂ = 0.088 mol L⁻¹]; [catalyst]: 1 mg mL⁻¹; [DBT in toluene]: 50 mg L⁻¹; [quinoline in toluene]: 50 mg L⁻¹.

Fig. 13. GC–MS chromatograms of standard and oxidized quinoline and DBT. Experimental conditions: $[H_2O_2 = 0.088 \text{ mol } L^{-1}]$; [catalyst]: 1 mg mL⁻¹; [DBT in toluene]: 50 mg L⁻¹; [quinoline in toluene]: 50 mg L⁻¹. *Column bleeding.

Fig. 13 shows the GC–MS chromatograms of the DBT–quinoline/toluene obtained before and after the oxidation experiment. The peaks corresponding to DBT and quinoline were identified by comparison of their retention time with references compounds while the peak of its corresponding sulfone was identified using a GC–MS and by comparison with an electronic mass spectrum library.

The model mixture of quinoline-DBT presents both peaks of N- and S-compounds (t=0 min, standard sample), but after 180 or 240 min of reaction time we observed that both compounds were oxidized considerably. The addition of DBT suppressed the performance of the Gli $400//H_2O_2$ in the oxidation of quinoline in approximately 50%. In order to investigate the mechanism of quinoline oxidation, the reaction products were extracted using methanol and analyzed by ESI-MS (Fig. 14). It was detected peaks with m/z = 201 related to hydroxylated DBT (DBT-OH) and m/z = 146 and 178 related to hydroxylated quinoline. These results confirm that the catalyst Gli 400 is very active to transfer oxygen species as •OH groups to DBT and quinoline molecules, which increase their polarity and permit the removal from fuel by partition using a polar solvent [34,35]. We proposed the structures for the oxidized compounds as shown in Fig. 15.

The difference in the activity of the materials may be related to the nature iron oxides phases and the presence of carbon islands present on the Gli 400. During the thermal treatment, glycerol mixed with α -FeOOH reduces the iron oxide surface to produce iron(II) species that are much more active in the generation of hydroxyl radicals. Moreover, the formation of elemental carbon can

Fig. 14. Analysis by ESI-MS of aqueous fraction extracted from the oxidation of DBT in the presence of quinoline.

give interesting characteristics to the iron oxide such as hydrophobicity increasing the catalytic activity. The scheme shown in Fig. 16 shows the biphasic reaction in the presence of natural limonite (a) and Gli 400 (b), suggesting the ability of the thermal treated material in remain in the interface of aqueous and apolar solvent.

Fig. 15. Proposal structures based on signals found in ESI-MS analyses.

Fig. 16. Scheme of biphasic reaction in the presence of natural limonite (a) and Gli 400 sample (b).

4. Conclusions

Glycerol was carbonized over the iron oxide surface at 400 °C under N_2 flow producing a hydrophobic carbon layer. Furthermore, the thermal decomposition of glycerol caused the formation of reduced iron species with high capacity to decompose hydrogen peroxide. The material can be easily recovered using a magnet device to be reused. The magnetic catalyst presented high catalytic activity for oxidation of quinoline and DBT in organic medium as showed by mass spectrometry analyses. We also observed an amphiphilic property for the reduced materials presenting a great potential for an ODS fuel treatment.

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