



Short communication

Amphiphilic catalysts based on onion-like carbon over magnetic iron oxide for petrochemical industry use

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ABSTRACT

Composites formed by carbon over magnetite were synthesized by impregnating iron oxide with glycerine. The formation of onion-like carbon was found, presenting concentric turbostratic shells with interplanar spacing of approximately 0.32 nm. The composite presented spherical iron oxide particles with magnetic and amphiphilic properties, which is interesting for use as a catalyst in the petrochemical industry. The magnetic composite presented a high catalytic activity for oxidation of quinoline in the aqueous and mainly in the organic medium.

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1. Introduction

Amphiphilic materials have been receiving attention because of their ability to simultaneously act in aqueous and organic mediums, which is used, for instance, in petrochemical processes [1,2]. Recently, an increasing demand for clean chemical process technologies in engineering can be observed, especially for removal of pollutant compounds. It is very well known that the sulfur and nitrogen impurities present in fuels are an important source of air pollution, acid rain and they also affect pollution control devices. In order to decrease pollution, new specifications for sulfur in diesel have been established in many countries [3–5]. Conventional hydrotreating (HDT) methods have been effective due to their ability to remove sulfur and nitrogen compounds, however, they are less competent for removing heterocyclic sulfur or nitrogen compounds such as dibenzothiophenes and quinolines, which are abundant especially in diesel [6–8]. Other processes have been studied in order to remove refractory HDS compounds. Oxidation (ODS) is a current process, which is based on the removal of the oxidized sulfur compounds from the hydrocarbon phase [9]. However, the ODS utilizes the homogenous process, which is a problem on the industrial scale because is not possible to separate the catalyst and product from the reaction mixture [10]. Therefore, heterogeneous catalytic oxidation using aqueous

H₂O₂ would be desirable. However, one serious problem in this system is the insufficient transfer of reagent molecules between the organic solvent and aqueous phase. Vigorous stirring to increase the apparent interface area could increase the reaction rate. However, the presence of a third component or co-solvent or the formation of an emulsion by stirring would make the workup procedure very complicated [11,6,12]. In order to increase the catalytic activity of the ODS in heterogeneous process is desirable to use catalysts with affinity for both aqueous and organic phases. We, therefore, present in this work an amphiphilic composite formed by iron oxide, which is a known catalyst for ODS process, covered by onion-like carbon.

2. Materials and methods

Carbon nanostructure was generated over the iron oxide by impregnation of glycerine followed by thermal treatment. Glycerol P.A. (811 mmol), and 5 g of natural goethite (obtained from Petrobras SA (Brazil)) were mixed in a 200 mL glass reactor, heated for 3 h until dry (150 °C) and then the system was heated in an oven at 10 °C min⁻¹ up to 500 °C for 1 h under N₂.

The quinoline oxidation (25 mg L⁻¹) with H₂O₂ (0.05 mol L⁻¹) at pH 6 (natural pH of the H₂O₂ solution) was carried out with a total volume of 10 mL using 10 mg of catalyst. All reactions were performed under magnetic stirring in a temperature-controlled bath kept at 25 ± 1 °C. Quinoline (10 mL) decomposition was monitored

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using electrospray ionization mass spectrometry (ESI-MS), in an attempt to identify the intermediately formed chemical species [9].

3. Results and discussion

Fig. 1 shows iron nanoparticles larger than 200 nm in diameter partially surrounded by a thick carbon shell. A fast Fourier transform of the enlarged HRTEM image revealed the spacing of the (002) lattice fringes of the carbon of approximately 3.2 nm. The close inspection of this enlarged images revealed some defects with well-ordered parts indicating that the carbon have a turbostratic carbon structure [13].

Fig. 2 shows the apparent distribution of raw iron oxide and the magnetic composite catalysts suspended in an aqueous toluene mixture.

Since the goethite species are hydrophilic and do not easily disperse in organic solvents, the goethite was dispersed well in the aqueous phase, as expected (Fig. 2a). It is worth noting that compared with goethite catalyst almost all of the magnetic composite particles were located at the aqueous–organic phase boundary (Fig. 2b). The characteristic behavior of modified material is attributable to its amphiphilicity generated by the presence of iron oxide and onion-like carbon composites.

It was observed by TEM image (Fig. 2c) that common acicular, polydomainic goethite crystals exist [14]. Moreover, typical core-shell structures of the magnetic composite were observed by TEM (Fig. 2d). The EDS results indicate that both catalysts before and after thermal treatment consist of Fe and O. In addition to Fe and O, the existence of carbon in the catalyst treated with glycerine can be observed. The carbon presence was due to decomposition of the glycerine after thermal treatment. Some impurities such as Ni, Al and Si were observed probably because of the natural origin of goethite. Beyond the amphiphilic properties of the composite it was observed that when placing the vial near an external magnet a progressive separation of magnetic composite was observed, while the catalyst was attracted toward the wall of the vial, which was closer to the magnet (Fig. 3b). With the time duration extending to 30 s, the suspension became clear (Fig. 3c). Furthermore, the catalyst powder can be re-dispersed again simply by shaking after removing the magnet. Hence, this kind of magnetic composite has the potential to be easily recovered after a liquid phase catalytic reaction, which could greatly facilitate the practical running of an industrial process.

298 K Mössbauer spectra for these materials are presented in Fig. 4. The raw goethite spectrum (Fig. 4a) can be fit with a hyperfine field distribution with maximum value of 32.0 T. This low hyperfine field value observed in our sample is due to superparamagnetic effects caused by structural defects and reduced magnetic coupling of iron due to cationic vacancies in the goethite structure [14,15]. The isomer shift of 0.36 mm s^{-1} show Fe^{3+} to be located on octahedrally-coordinated sites. The doublet with isomer shift of 0.37 mm s^{-1} and quadrupole splitting of 0.60 mm s^{-1} can be assigned to iron oxides with small particle size. After

treatment, two sextets can be observed (Fig. 4b) with hyperfine field of 43.8 T and 47.6 T, which can be assigned to $\text{Fe}^{2.5+}$ on octahedral (B) site and Fe^{3+} on tetrahedral (A) site in the magnetite structure, respectively. The superparamagnetic relaxation and some collective excitation effects caused the decreasing of the hyperfine field in respect to magnetite bulk. Moreover, the significant line broadening and asymmetric line shapes observed in the spectrum of Fig. 4b are due to these effects. The presence of magnetite in the magnetic composite suggests that goethite was converted into magnetite to form the magnetic support for hydrophilic carbon in the composite.

In order to confirm the presence of goethite and magnetite in the samples Mössbauer measurements at 110 K were performed. The Mössbauer spectrum of raw goethite (Fig. 4c) showed a unique sextet with hyperfine field of 49.0 T and quadrupole shift of -0.23 mm s^{-1} characteristic of goethite. On the other hand, two sextets could be observed for the magnetic composite. One, with a hyperfine field of 49.9 T, quadrupole shift of 0.01 mm s^{-1} and isomer shift of 0.67 mm s^{-1} is typical of $\text{Fe}^{2.5+}$ in the magnetite structure, indicating that magnetite does not undergo Verwey transition. The transition is very sensitive to structure defects, stoichiometry, impurity content, vacancies, stored stresses and particle sizes [16]. Another sextet (Fig. 4d) with a hyperfine field of 50.3 T, quadrupole shift of -0.05 mm s^{-1} and isomer shift of 0.35 mm s^{-1} corresponds to Fe^{3+} in tetrahedral coordination in the magnetite structure. These results confirm that all goethite was converted into magnetite during the synthesis process.

The catalytic activity of the samples was studied using two reactions: (i) the H_2O_2 decomposition and (ii) the oxidation of quinoline with H_2O_2 in aqueous medium and in toluene. The conversion was monitored by GC–MS (Gas-chromatograph Mass Spectrometry) and the intermediates formation by ESI-MS (Electrospray Ionization Mass Spectrometry).

It is observed that raw iron oxide and the nanocomposite favored the H_2O_2 decomposition, probably due to presence of goethite and magnetite phases on the surface as observed by Mössbauer spectroscopy. In fact, those iron oxide phases are widely used in the hydrogen peroxide decomposition to produce the hydroxyl radical in heterogeneous Fenton reaction because the redox reaction involving the Fe^{3+} and/or Fe^{2+} and H_2O_2 is facilitated [17]. Moreover, the catalytic test for quinoline (a diesel contaminant model molecule) oxidation in water or toluene showed high catalytic activity in toluene medium, after incorporation of carbon on the iron oxide forming the nanocomposite. The raw material with hydrophilic properties was more efficient in aqueous medium (57% of conversion) while the magnetic composite presented higher conversion in toluene (93%). The data are summarized in Table 1. These results clearly show the amphiphilic properties of the material after thermal treatment with glycerine. This new catalyst, that was very active removing almost all of the quinoline, can be used in petrochemical processes to eliminate nitrogen-compounds from diesel.

The ESI-MS spectrum obtained (not shown here) for the quinoline solution shows only a strong signal at $m/z = 130$ (m /

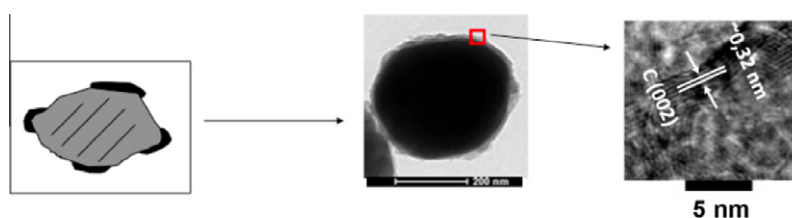


Fig. 1. HR-TEM image of magnetic iron oxide and carbon composite and a partial magnification image of carbon on the surface.

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