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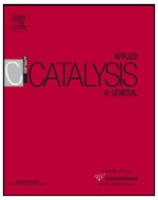

Effect of Ni incorporation into goethite in the catalytic activity for the oxidation of nitrogen compounds in petroleum

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ABSTRACT

Samples of Ni-doped goethites were prepared and characterized by Mössbauer spectroscopy, IV, XRD, TPR and BET surface area measurements. Mössbauer data evidenced the incorporation of Ni^{2+} in the goethite structure, and this cation-doping caused a significant decrease of the chemical reduction temperature in the TPR process. The catalytic behavior of these $Fe_{1-x}Ni_xOOH$ materials was investigated for the H_2O_2 decomposition to O_2 and the oxidation of quinoline. The successive hydroxylation of quinoline during this oxidation strongly suggests that highly reactive hydroxyl radicals are generated during the reaction involving H_2O_2 on the Ni-goethite grain surface, also confirming that these materials are efficient heterogeneous Fenton catalysts.

1. Introduction

Many iron oxides play an important role in a variety of disciplines and also serve as a model system of reduction and catalytic reactions [1–3]. Goethite (α-FeOOH) is commonly used as an adsorbent [4,5], a catalyst precursor and an active component of catalytic material [6–9]. The special importance of goethite (α-FeOOH) results from the combination of its ubiquitous presence in soils and sediments and its exceptional chemical reactivity. The goethite is a poorly and imperfectly crystallized material having a large surface area. These characteristics and its open channel structure result in an unusual capacity to incorporate, adsorb, and fix ions from migrating solutions [10].

Various metal cations can be incorporated into the α-FeOOH structure, and many researchers have focused on the influence of the doping of α-FeOOH on its chemical, microstructural and physical properties [11]. The properties of these iron oxides, such as their saturation magnetization and magnetocrystalline anisotropy constants, strongly depend on the kind and the amount of substituting metal ions [12]. It is well know 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; e.g., in the Brazil a sulfur concentration of less than 50 ppm has been established for 2010 and for 2013 a sulfur concentration less than 10 ppm. In this context, clean fuels research, including desulfurization and denitrogenation, has become an important subject of environmental catalysis studies worldwide [13]. Conventional hydrotreating (HDT) methods have been effective for the easy-to-remove sulfur and nitrogen compounds, while less competent for removing heterocyclic sulfur or nitrogen compounds (such as dibenzothiophenes and quinolines) which are abundant especially in diesel [14]. Other processes have been studied in order to remove refractory HDS compounds. Oxidesulfurization (ODS) is a current process and has been discussed recently where the oxidized sulfur compounds can be removed from the hydrocarbon phase by extraction or precipitation. The sulfones are highly polar compounds and are easily separated from the fuel product by extraction during ODS process [15]. Another important factor in the ODS process is to evaluate the effect of other compounds present in the oil fractions. The majority of heteroatom-containing compounds of crude oil, especially nitrogen-containing compounds, still exist in the residual oil and these nitrogen compounds that coexist in distillate oil medium can inhibit the ultra-deep HDS [16]. Meanwhile, the removal of such nitrogen compounds from the middle-distillate oil can improve significantly the ultra-deep HDS performance. In addition, nitrogen compounds in the fuel and NH_3 produced during hydrocarbon reforming process are also to the catalysts. Besides they are harmful not only to the ODS process, but also to the stability of oil. Therefore it is strongly desired that most nitrogen-containing com-

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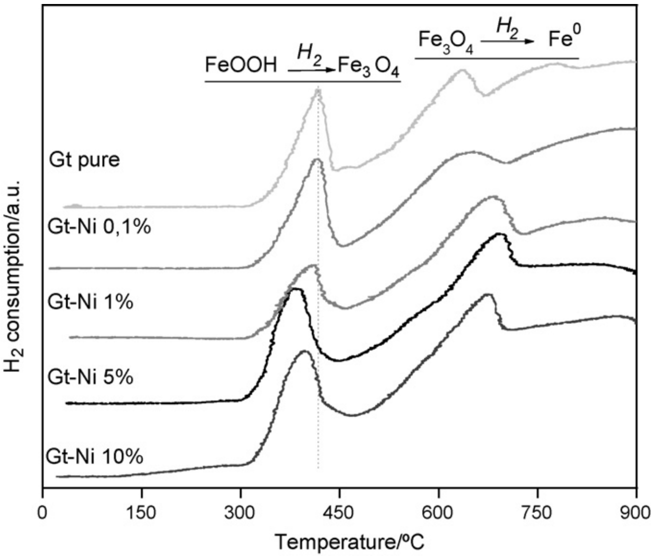

Fig. 1. Temperature-programmed reduction profile of the materials.

pounds be removed when processing residual oil, but the reduction of refractory heteroatom-containing compounds is marginal [16].

Now it is necessary to develop new approaches to ultra-deep desulfurization and denitrogenation for diesel fuel [14]. Several studies have recently been published involving different iron species for the removal of these contaminants from crude oil [4,5,17]. Recently, a Fenton-like system that combines H_2O_2 and limonite ore as catalyst was developed [17]. This combined aqueous slurry system is able to perform oil phase oxidation and simultaneous removal of unstable hydrocarbons and heteroatom compounds from hydrocarbon streams, such as Petroleum distillates. In the present work, we have focused on the influence of Ni-dopant on the properties of α-FeOOH particles precipitated in highly alkaline media. This study proposes yet to evaluate the oxidation of quinoline as representative model compound of heteroatom molecule present in diesel, aiming at a possible elucidation of the reaction mechanisms involved.

2. Experimental

2.1. Catalyst preparation and characterization

All chemicals were high purity grade and were used as purchased. A goethite sample was prepared by co-precipitation, starting from $Fe(NO_3)_3 \cdot 6H_2O$ ($1.7\,\mathrm{mol\,L^{-1}}$) and NaOH ($1\,\mathrm{mol\,L^{-1}}$) followed by thermal treatment at 60 °C (72 h). The Ni-substituted goethites (GtNi) were prepared from $Fe(NO_3) \cdot 6H_2O$ ($1.7\,\mathrm{mol\,L^{-1}}$) and $NiSO_4$ (Merck) solution by precipitation with sodium hydroxide ($1.0\,\mathrm{mol\,L^{-1}}$). The concentration of Ni ions in the doped goethite was targeted to be between 0.1 and 10%. The precipitates were washed with water until pH 7, dried at 80 °C for 12 h. The synthetic samples were then ground and sieved to 100 mesh (Tyler series), dried for 1 h at 120 °C. The surface area was determined with the BET method using N_2 adsorption/desorption in an Autosorb 1 Quantachrome instrument. Mössbauer spectroscopy experiments were carried out at room temperature in a spectrometer model MA250 with a 57Co/Rh source, using an 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° 2θ at a scan rate of $48\,\mathrm{min^{-1}}$. TPR experiments were performed in a CHEMBET 3000 equipment with 40 mg sample under $80\,\mathrm{mL\,min^{-1}}$ $H_2(5\%)/N_2$ with heating rate of $10\,^{\circ}\mathrm{C\,min^{-1}}$. Pure and GtNi samples were analysed by FTIR using an Excalibur FTS 3000 from BioRad. The specimens were pressed into small discs using a spectroscopically pure KBr matrix.

2.2. Catalytic tests

To perform oxidation tests, 2 mL of H_2O_2 (VETEC, 50%, v/v) and 30 mg of these goethite samples were added to 3.5 mL of Millipore MilliQ water under stirring and nearly constant temperature, at 25 °C. The catalytic properties of the material were tested via oxida-

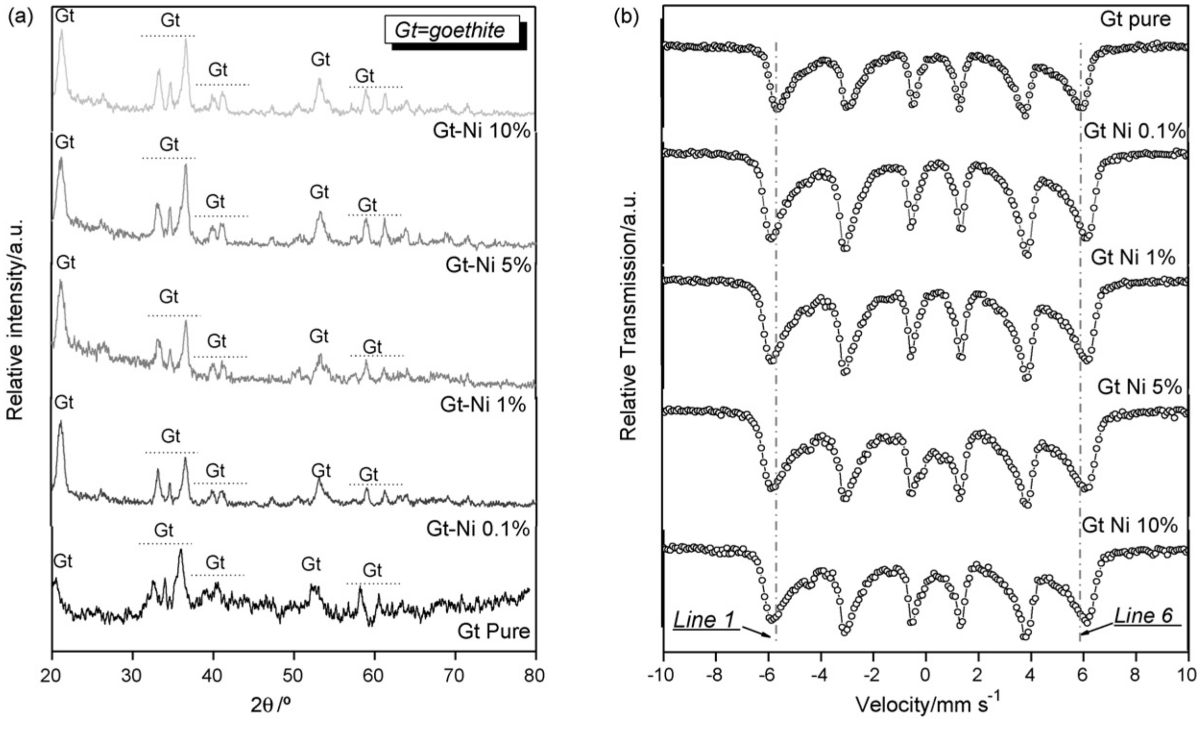

Fig. 2. XRD patterns (a) and Mössbauer spectroscopy (b) of samples Gt pure and Ni-doped goethites (Gt = goethite).