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Niobian iron oxides as heterogeneous Fenton catalysts for environmental remediation

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Abstract Heterogeneous Fenton or Fenton-like reagents consist of a mixture of an iron-containing solid matrix and a liquid medium with H_2O_2. The Fenton system is based on the reaction between Fe^{2+} and H_2O_2 to produce highly reactive intermediate hydroxyl radicals ($^{\bullet}OH$), which are able to oxidize organic contaminants, whereas the Fenton-like reaction is based on the reaction between Fe^{3+} and H_2O_2. These heterogeneous systems offer several advantages over their homogeneous counterparts, such as no sludge formation, operation at near-neutral pH and the possibility of recycling the iron promoter. Some doping transition cations in the iron oxide structure are believed to enhance the catalytic efficiency for the oxidation of organic substrates in water. In this work, goethites synthesized in presence of niobium served as precursors for the preparation of magnetites (niobian magnetites) via chemical reduction with hydrogen at 400°C. These materials were used as Fenton-like catalysts. Both groups of (Nb, Fe)-oxide samples were characterized by ^{57}Fe Mössbauer spectroscopy at 298 K. The results show that increasing niobium contents raise the catalytic potential for decomposition of methylene blue, which was, in this work, used as a model molecule for organic substrates in water.

Keywords Magnetite · Niobium · Fenton reaction

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1 Introduction

Spinel iron oxides are of technological importance because of their structural, electronic, magnetic and catalytic properties [1]. Other metal cations can isomorphously replace iron in magnetite (Fe_3O_4), thereby changing selected physico-chemical properties of the material, depending on the nature and amount of the metal and on the structural site on which the metal is incorporated [1].

A novel and promising catalytic application of iron oxides is the chemical decomposition of organic contaminants in wastewaters, using H_2O_2 in a heterogeneous Fenton system [2–6]. In this heterogeneous Fenton system the iron oxide activates H_2O_2 to generate radicals, especially $^\bullet OH$, which can completely oxidize organics present in the aqueous medium [7]. Magnetite has been observed to be particularly active for the Fenton oxidation of organics by H_2O_2. This activity was assigned to the presence of Fe^{2+} species in the magnetite structure, which can activate H_2O_2 by a Haber–Weiss mechanism [8]. Recent work has shown that the activity of magnetite is strongly influenced by the presence of different metals in the spinel structure. Thus the introduction of cobalt and manganese in the magnetite structure remarkably increased the reactivity towards the Fenton chemistry, whereas nickel showed an inhibitory effect [9–11].

In this work, niobium associated with magnetite (“niobian magnetite”) has been used to produce an active heterogeneous spinel system. Nb^{5+} shows interesting features for this system such as an ionic radius (64 pm in octahedral coordination) [12] that is comparable to that of high-spin octahedral Fe^{3+} (65 pm) and, based alone on size, might be structurally incorporated in magnetite, and a high reactivity towards H_2O_2 activation. To our knowledge, no systematic studies on iron-rich spinels prepared in a niobium-containing medium or their catalytic properties have been reported so far.

2 Experimental

2.1 Synthesis and characterization

The goethite samples were prepared by precipitation of $Fe(NO_3)_3 \cdot 6H_2O$ (1 mol L^{-1}) with potassium hydroxide (5 mol L^{-1}) and the addition of 2, 7 and 17 mol% niobium that is present in $NH_4[NbO(C_2O_4)_2(H_2O)](H_2O)_n$ supplied by CBMM (Araxá, MG, Brazil). The precipitates were washed with water until the pH became adjusted to 7; they were then transferred to a 2 L-beaker with distilled water and aged for 72 h at 60°C. The so produced goethites were finally reduced with hydrogen for 30 min at 400°C to produce magnetites.

The total iron was determined by $K_2Cr_2O_7$ titration and energy dispersive spectrometry (EDS) analyses were performed using a Jeol JXA-8900RL microscope. Mössbauer spectra were taken at room temperature (298 K) on a CMTE MA250 spectrometer with a constant acceleration drive and a $^{57}Co/Rh$ source at room temperature. The experimental data were fitted using Lorentzian functions with a least-squares procedure based on the NORMOS program, and calibration was effected and isomer shifts are given relative to α-Fe. Powder X-ray diffraction (XRD) was carried out on a Rigaku Geigerflex 3064 diffractometer equipped with

Table 1 Compositions of the niobian magnetites from chemical analyses and EDS data

Sample	Total Fe/%	Nb/%
(a) Pure Mt	70(3)	0
(b) Mt-Nb2	67(1)	2.1(2)
(c) Mt-Nb7	61(1)	7(1)
(d) Mt-Nb17	59(1)	17(2)

a Cu tube and a graphite diffracted-beam monochromator. To improve accuracy, additional scans of the samples were taken with Si as internal standard.

2.2 Reactions

The hydrogen peroxide decomposition was carried out by mixing 10 mL H_2O_2 2.9 mol L^{-1} and 10 mg catalyst and measuring the formed gaseous O_2 in a volumetric glass system. The oxidation of the methylene blue dye (50 mg L^{-1}) with H_2O_2 (0.3 mol L^{-1}) at pH 6.0 (the pH of the sole H_2O_2 solution) was carried out with a total volume of 10 mL and 10 mg of the oxide catalyst. The reactions were monitored by UV–vis measurements. All reactions were carried out under magnetic stirring in a recirculating controlled-temperature bath kept at $25 \pm 1°C$.

In an attempt to identify the intermediate products, the decomposition of methylene blue was also monitored with the positive ion mode ESI-MS in an Agilent MS-ion trap mass spectrometer (1100 Series). The reaction samples were analyzed by introducing aliquots into the ESI source with a syringe pump at a flow rate of 5 L min^{-1}. The spectra were obtained as an average of five scans of 0.2 s each. Typical ESI conditions were as follows: heated capillary temperature 325°C; sheath gas (N_2) at a flow rate of 20 units (ca. 4 L min^{-1}); spray voltage 4 kV; capillary voltage 25 V; tube lens offset voltage 25 V.

3 Results and discussion

3.1 Characterization of materials

Not unexpectedly, the chemical compositions of the niobian magnetites (Table 1) show a concurrent increase of niobium and decrease of iron.

Room-temperature Mössbauer spectra of the unsubstituted magnetite and the niobian series are shown in Fig. 1. While spectra of the pure magnetite and the samples prepared in presence of 2 and 7 mol% niobium show two characteristic sextets that can be assigned to Fe^{3+} on the A sites and Fe^{2+}/Fe^{3+} on the B sites of magnetite [13], the sample prepared in the presence of 17 mol% niobium shows only a minor indication of magnetite.

Analysis of the Mössbauer spectra (Table 2) shows the tetrahedral (A site) of the unsubstituted magnetite to have a hyperfine field (B_{hf}) of 49.0 T and the B (octahedral) site to have a hyperfine field of 45.8 T with isomer shifts (δ) relative to α-Fe of 0.28 and 0.67 mm s^{-1}, respectively. While these parameters resemble those of pure, stoichiometric magnetite [13], the area ratio of the B-site resonance to that of the A-site resonance (1.39) indicates the unsubstituted magnetite to have a composition given by $Fe_{2.94}O_4$, and thus to have undergone noticeable oxidation.

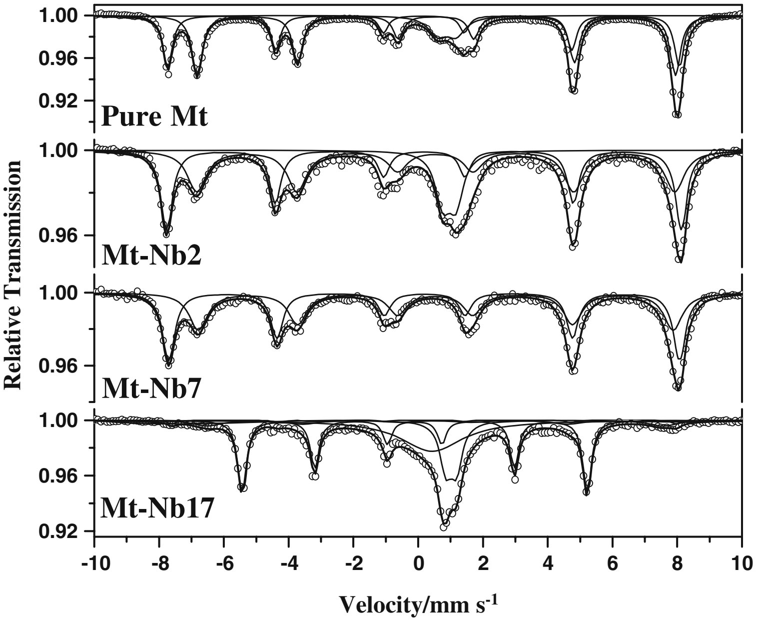

Fig. 1 Room-temperature Mössbauer spectra of the niobian magnetites

Table 2 Room-temperature (~298 K) Mössbauer parameters for pure magnetite and magnetites prepared in the presence of niobium

Sample	^{57}Fe site	δ/mm s^{-1}	2ε, Δ/mm s^{-1}	B_{hf}/T	Γ/mm s^{-1}	RA/%
Pure Mt	A	0.2831(8)	−0.010(1)	48.960(6)	0.349(2)	36.6(2)
	B	0.6680(7)	0.010(1)	45.786(5)	0.388(2)	50.8(2)
	Fe^{2+}	1.000(4)	0.571(7)	–	0.70[a]	12.6(1)
Mt-Nb2	A	0.295(2)	−0.013(3)	49.27(1)	0.433(5)	40.6(4)
	B	0.649(3)	0.012(6)	45.75(2)	0.72(1)	43.5(1)
	Fe^{2+}	1.076(3)	0.408(6)	–	0.55[a]	15.9(1)
Mt-Nb7	A	0.304(3)	−0.020(5)	48.90(2)	0.458(9)	50(1)
	B	0.642(5)	0.020(9)	45.46(4)	0.69(2)	50(1)
Mt-Nb17	A	0.30[a]	−0.02[a]	48.2(1)	0.42(6)	3.0(4)
	B	0.63[a]	0[a]	43.7(1)	0.71[a]	7.2(3)
	Fe^{2+}	1.124(3)	0.326(4)	–	0.42(1)	16.6(5)
	Fe^0	−0.0020(8)	0[a]	33.034(6)	0.323(3)	41.0(3)
	Doublet	0.59(2)	0[a]	–	2.29(4)	32.2(6)

δ isomer shift relative to α-Fe, 2ε quadrupole shift, Δ quadrupole splitting, B_{hf} magnetic hyperfine field, RA: relative sub-spectral area

[a] Parameter held fixed during fitting

The degree of oxidation rises with increasing niobium concentration during synthesis from the above value to $Fe_{2.92}O_4$ at 2% niobium in the synthesis solution and to $Fe_{2.91}O_4$ at 7% niobium. The line widths of the magnetites prepared in the presence of niobium, particularly those of the B sites, are furthermore significantly higher

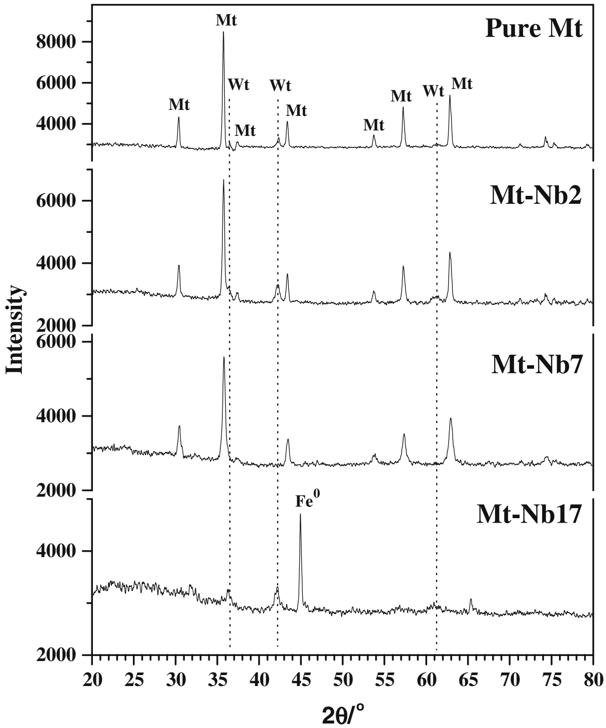

Fig. 2 X-ray diffraction diagrams of the niobian magnetites

than those of the pure magnetite. At a niobium concentration of 17%, magnetite formation is largely inhibited, but the Mössbauer spectrum indicates the presence of magnetically ordered metallic iron and paramagnetic Fe^{2+}. The magnetic hyperfine fields of the A site show no and the B-fields show little systematic variation as a function of the niobium concentration during synthesis. Because Nb^{5+} is a diamagnetic ion with a krypton configuration, this does not provide conclusive evidence for the concept that niobium has substituted iron in the magnetite structure. The lines of the magnetite components become broader as the concentration of niobium in the synthesis solution increases, indicating decreasing particle sizes. Mean coherence lengths calculated from broadening of the 311 diffraction line indicates a significant decrease from 62 to 45, 24 and 8 nm from the pure magnetite to the 2%, 7%, and 17% Nb samples, respectively.

Powder XRD (Fig. 2) also shows the samples to contain various proportions of magnetite (the sample prepared in the presence of 17% niobium again showing the lowest proportion of magnetite), and the samples prepared in the presence of 2% and 17% niobium show the presence of some wüstite ($Fe_{1-x}O$). Diffraction diagrams (not shown) were also taken under addition of Si as an internal standard for 2θ. The resulting patterns do not show a systematic variation of the position of the strongest magnetite peak (311) as a function of the niobium concentration, so that XRD also does not provide conclusive evidence for the incorporation of niobium in the magnetite structure.

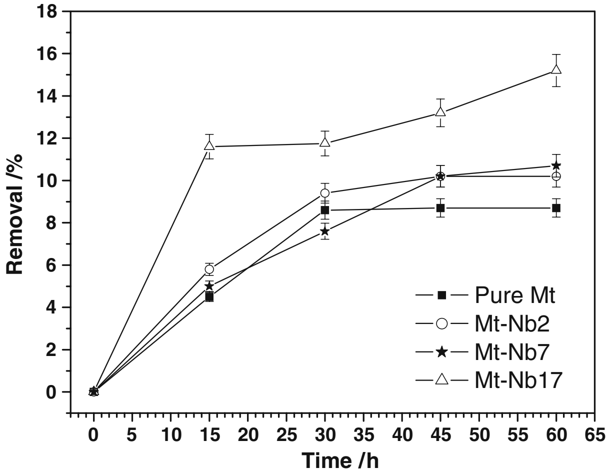

Fig. 3 Methylene blue discoloration in the presence of niobian magnetites

3.2 H_2O_2 decomposition and dye oxidation

The catalytic activity of the niobian magnetites was studied using two reactions: (1) the decomposition of H_2O_2 to O_2 ($H_2O_2 \rightarrow H_2O + 0.5\ O_2$) and (2) the oxidation of the model contaminant (methylene blue dye) with H_2O_2 in an aqueous medium. The reaction kinetics was investigated by UV/vis discoloration measurements to form non-colored intermediates. The discoloration of the solution of the dye is shown in Fig. 3.

The control experiment (only methylene blue and H_2O_2 but no catalyst) showed no significant discoloration even after a reaction time of 60 min. On the other hand, in the presence of the niobian magnetite catalyst and H_2O_2 as oxidant, discoloration can be observed. For the system niobian magnetite/H_2O_2, the discoloration is moderate in the presence of the pure magnetite and the magnetites prepared at low niobium contents. However, the sample prepared at high niobium content (Mt-Nb17) produces a catalytic discoloration of more than 15% after 60 min. This behavior can have several causes: sample mineralogy (e.g. the presence of metallic iron in the Mt-Nb17 sample), a catalytic enhancement due to the presence of Nb, and particle size changes. While some or all of these effects can act together to bring about the higher catalytic activity of the Mt-Nb17 sample, the drastic particle size reduction of magnetite in this sample indicates particle size to play a key role. Although H_2O_2 decomposition kinetics is a complex reaction, the linear behavior of the decomposition plots between 0 and 25 min suggests that the process can be approximated to pseudo-zero order kinetics [8].

Discoloration measured by UV–vis spectroscopy does not provide any information about reaction intermediates of the methylene blue oxidation. Such identification could be achieved by using mass spectroscopy with electrospray ionization. The identification of intermediates was studied obtaining spectra after 60 min of reaction in the presence of H_2O_2 (Fig. 4). The spectrum of methylene blue solution (without catalysts) indicated only one peak at $m/z = 284$ due to its cationic structure. After 1 h of reaction, intermediates were observed in the spectra, showing that the mineralization was not total. An intense peak at $m/z = 270$ suggested the beginning

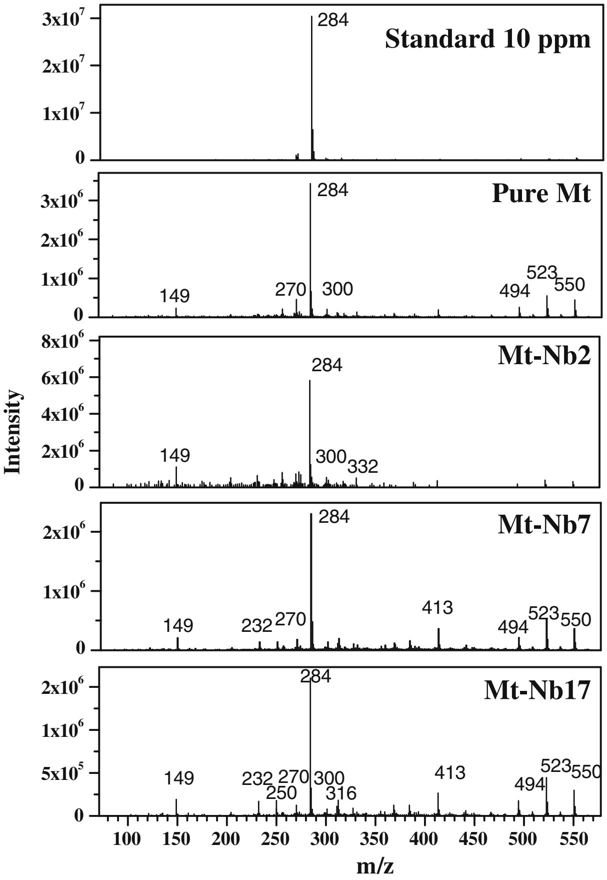

Fig. 4 Mass spectra of the reaction products of methylene blue oxidation with electrospray ionization as a function of the niobium concentration

of dye structure degradation. A signal at $m/z = 300$ and 316 is probably due to successive hydroxylation of the aromatic ring [14]. The peak at $m/z = 149$ is indicative of ring rupture and subsequent total mineralization [15].

4 Conclusions

The presence of niobium associated with magnetite has a significant effect on the crystallinity and catalytic activity of the oxide. In this study, the oxidation of organic compounds with H_2O_2 has been shown to probably take place via radicals, as suggested by ESI-MS data. An oxidation mechanism was indicated to occur by attack of the free radical *OH over the molecule, giving rise to hydroxylation products as principal by-products, although compounds resulting from ring cleavage are also detected. The presence of niobium increases the activity of the oxide for the H_2O_2 decomposition, and the surface niobian species seem to act directly in the catalytic properties of the niobian magnetites.

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