# Formation of Highly Reactive Species at the Interface Fe°–Iron Oxides Particles by Mechanical Alloying and Thermal Treatment: Potential Application in Environmental Remediation Processes

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In this work, the formation of highly reactive species at the interface of Fe°/iron oxides mixtures, i.e., $Fe_3O_4$, $\gamma$-$Fe_2O_3$, or $\alpha$-$Fe_2O_3$ prepared by mechanical alloying and thermal treatment at 200–800 °C was studied. Mössbauer spectroscopic, XRD, SEM, BET, and magnetization measurements suggest a strong interaction between the metal and the oxides producing highly reactive surface species which can readily react with gas phases, i.e., $O_2$, and with aqueous phase, i.e., $H_2O_2$, molecules.

Iron metal, a low cost and an innocuous reductant, has been intensively investigated in recent years for several environmental remediation processes,[1] e.g., permeable reactive barrier, reduction of organochloro, nitroaromatic compounds, dyes, pesticides, nitrate/nitrite, Cr(VI), Hg(II), and As. Also, different iron compounds, such as Fe°, $Fe_3O_4$, $Fe_2O_3$, and FeOOH, have been reported to promote the Fenton reaction. All these processes involve multiphase heterogeneous systems where the rate is controlled by surface properties and interface phenomena. A great challenge in this area is to produce more active and more stable systems to improve the efficiency and widen the application in environmental remediation processes. Several approaches have been used to increase the activity of these systems, such as sonication, external voltage, bimetallic systems Ni/Fe and Pd/Fe, and the use of iron nanoparticles.

In this work, a unique effect on the reactivity of mechanical alloyed and thermally treated Fe°/iron oxides mixtures, i.e. $Fe_3O_4$, $\alpha$-$Fe_2O_3$, and $\gamma$-$Fe_2O_3$ is reported. These treatments result in the formation of highly reactive surface species towards electron transfer to molecules in the gas phase, i.e., $O_2$, and in aqueous phase, i.e., $H_2O_2$.

The mixtures were prepared from $\alpha$-Fe (Sicalab) and iron oxides powders[2] (wt ratio; Fe:oxide = 1:1) mechanically alloyed by manual grinding for 60 s. Upon mechanical alloying of the mixture Fe°/$Fe_3O_4$ by manual grinding for 60 s no significant difference was observed in the Mössbauer spectrum (MS) (CMTE model MA250 $^{57}$Co/Rh at 25 °C, $\alpha$-Fe as reference) and the XRD (Rigaku model Geigerflex at 4° $min^{-1}$) of the Fe° and $Fe_3O_4$ phases. On the other hand, SEM (Jeol JKA 8900RL) showed that the metal and the oxide particles (ca. 15–50 and 20–100 µm, respectively) remarkably change the texture after mechanical alloying producing agglomerates of small particles.

The thermal treatments were carried out under Ar (99.995%) at 10 °C $min^{-1}$ to 200, 400, 600, or 800 °C for 2 h and quenching to room temperature. The samples were transferred to vials (exposition to air occurred in this step), kept under $N_2$ and analyzed by MS immediately. The phase compositions obtained from the MS data of the mixtures Fe°/$Fe_3O_4$ treated at different temperatures are shown in Figure 1.

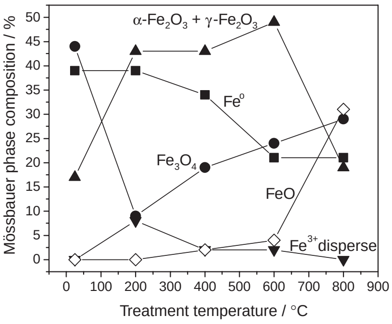

**Figure 1.** Mössbauer phase composition of mixtures Fe°/$Fe_3O_4$ thermally treated at 200–800 °C.

Upon thermal treatment at 200 °C a strong decrease on the $Fe_3O_4$ relative concentration, from 44 to 9% with a concomitant increase on the oxidized phases $Fe^{3+}{}_{dispersed}$, $\alpha$- and $\gamma$-$Fe_2O_3$ can be observed. It is interesting to observe that these oxidized products could not be formed by the reaction of the Fe° with magnetite under an argon atmosphere. This result can only be explained by an oxidation after the treatment when the mixture was exposed to air. In fact, the mixture treated at 200 °C in a sealed ampoule and not exposed to air showed no significant change in the MS. These results strongly suggest that the thermal treatment of the Fe°/$Fe_3O_4$ mixture at 200 °C does not cause a significant bulk change but it is likely producing very reactive surface species. These surface species can react with $O_2$ when exposed to air even at room temperature by an exothermic reaction to form the phases $Fe_2O_3$. No significant change was observed in the concentration of Fe° indicating that magnetite was the phase oxidized (Eqs 1 and 2).

$$\mathrm{Fe^\circ/Fe_3O_4\ (200\,^\circ C)} \rightarrow \text{“}\mathrm{Fe_3O_4}\text{” reactive,} \tag{1}$$

$$\text{“}\mathrm{Fe_3O_4}\text{” reactive} + \mathrm{O_2\ (air)} \rightarrow \mathrm{Fe_2O_3}. \tag{2}$$

Also, experiments with pure Fe° and pure $Fe_3O_4$ (not mixed) ground and thermally treated at 200 °C did not show any significant difference in MS, reinforcing that interaction between the phases is important for the observed reactivity.

At 400 and 600 °C the Fe° relative concentration decreases, suggesting a significant reaction with $Fe_3O_4$ during thermal treatment, likely by the surface reaction to form $Fe^{+2}$ species, such as wüstite:

$$\mathrm{Fe^\circ} + \mathrm{Fe_3O_4} \rightarrow 4\ \mathrm{FeO}. \tag{3}$$

The treatment at 800 °C leads to the formation of the $Fe_{1-x}O$

(wüstite), which was clearly identified by MS and XRD.

These phase reactions are also reflected in the bulk magnetization measurements, which decreased from 99 to 50 $\mathrm{J\,T^{-1}\,kg^{-1}}$ and surface area (Autosorb 1 Quantachrome) which reduced from 16 to 1 $\mathrm{m^2\,g^{-1}}$ when the mixture was treated at 800 °C. Similar MS, XRD, and BET results were obtained for the mixtures $Fe^\circ/\alpha\text{-}Fe_2O_3$ and $Fe^\circ/\gamma\text{-}Fe_2O_3$.

The reactivity of the treated $Fe^\circ/Fe_3O_4$ mixtures was studied by the decomposition reaction of $H_2O_2$ which is a versatile probe reaction to investigate the activity of heterogeneous systems towards the Fenton chemistry.

$$H_2O_2(aq) \rightarrow H_2O(l) + 1/2O_2(g). \qquad (4)$$

Under the reaction conditions studied ($[H_2O_2] = 2.7$ $\mathrm{mol\,L^{-1}}$, 10 mL, 60 mg $Fe^\circ/Fe_3O_4$) the decomposition showed a pseudo-zeroth-order behavior with rate constant ($k_{obs}$) for the mixtures treated at different temperatures shown in Figure 2.

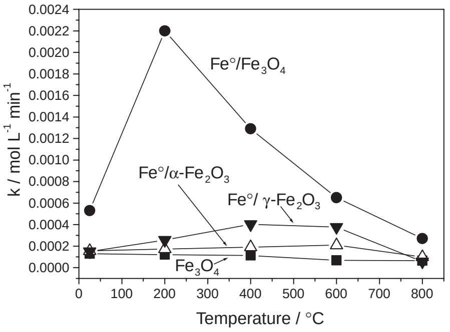

**Figure 2.** Hydrogen peroxide decomposition rate in the presence of thermally treated mixtures: $Fe^\circ/Fe_3O_4$, $Fe^\circ/\alpha\text{-}Fe_2O_3$, $Fe^\circ/\gamma\text{-}Fe_2O_3$, and pure $Fe_3O_4$ ($25 \pm 1$ °C, 7 mL $[H_2O_2]$ 2.7 $\mathrm{mol\,L^{-1}}$, 60 mg of the mixture).

It can be observed that thermal treatment at 200 °C produces a remarkable increase in the activity for the peroxide decomposition with $k_{obs}$ $22 \times 10^{-4}\ \mathrm{mol\,L^{-1}\,min^{-1}}$. As the sample was treated at higher temperatures, the activity decreased progressively. Much lower $k_{obs}$ peroxide decomposition rate constants were observed for the $Fe^\circ/\alpha\text{-}Fe_2O_3$ and $Fe^\circ/\gamma\text{-}Fe_2O_3$ mixtures.

The results presented in this work suggest that the mechanical alloying and thermal treatment of the mixtures $Fe^\circ/Fe_3O_4$ produce very reactive species. Both reactions studied, i.e., with $O_2$ and $H_2O_2$, are likely electron-transferring processes, i.e.[3]

$$\begin{aligned} &O_2(surf) + e^- \rightarrow O_2{}^-(surf) + e^- \\ &\quad \rightarrow O_2{}^{2-}(surf) + e^- \rightarrow O^{2-}(surf), \end{aligned} \qquad (5)$$

$$H_2O_2 + e^- \rightarrow HO^- + HO^*, \qquad (6)$$

$$HO^* + H_2O_2 \rightarrow HOO^* \rightarrow H^+ + O_2 + e^-. \qquad (7)$$

The formation of these reductive reactive species involves the reaction of the phases Fe° and $Fe_3O_4$, and likely takes place by an electron transfer from the metal to the magnetite, probably to $Fe^{3+}{}_{magnetite}$. This process should be thermodynamically favorable as suggested by the eq:

$$Fe^\circ + 2Fe^{3+} \rightarrow 3Fe^{2+} \quad \Delta E^\circ = 1.21\ \mathrm{V}. \qquad (8)$$

The octahedric site in the magnetite spinel structure is a very versatile redox site which can accommodate both $Fe^{3+}$ and $Fe^{2+}$. Therefore, the $Fe^{3+}{}_{oct}$ can be easily reduced to $Fe^{2+}{}_{oct}$ with no structural constrain:

$$\begin{aligned} &[Fe^{3+}]_{tet}[(Fe^{3+})_1(Fe^{2+})_1]_{oct}O_4 + ne^- \rightarrow \\ &\qquad [Fe^{3+}]_{tet}[(Fe^{3+})_{1-n}(Fe^{2+})_{1+n}]_{oct}O_{4-n/2}. \end{aligned} \qquad (9)$$

The reduced magnetite should also show higher concentration of oxygen vacancies[4] which are reducing sites and can promote both the reactions, with $O_2$ and $H_2O_2$.[5] Magnetite, a semiconductor with a narrow band gap (0.1 eV) and very high conductivity (almost metallic, ca. $10^2$–$10^3\ \Omega^{-1}\,\mathrm{cm^{-1}}$)[6] should also favor electron transport in this system. The efficient interface, electron transport and reaction between Fe° and the oxide have been clearly observed by X-ray absorption spectroscopy.[7] Another product that can be formed at the interface of alloyed $Fe^\circ/Fe_3O_4$ is wüstite, $Fe_{1-x}O$.[8] Wüstite is a metastable phase[9] and tends to disproportionate into α-Fe° and $Fe_3O_4$, below its eutectoid temperature, 570 °C.[10] Depending on the conditions of its formation and decomposition, wüstite can produce highly dispersed nanoparticles of Fe° and $Fe_3O_4$.[11] On the basis of these results, one can consider that if wüstite is formed at the interface $Fe^\circ/Fe_3O_4$ by the mechanical alloying, it can decompose, at room temperature or during the thermal treatment at 200–400 °C to form highly dispersed iron phases. These highly dispersed reactive iron phases will also readily react with $O_2$ to form $Fe_2O_3$ upon exposure to air. The mixtures $Fe^\circ/Fe_3O_4$ treated at 800 °C showed the reaction of Fe° with the oxide to wüstite. At this temperature a more well-crystallized and stable wüstite phase is likely formed and the strong sintering (as observed by SEM and BET) leading to the encapsulation of particles will protect the phases from the $O_2$ of air. It is interesting to observe that reactive systems towards $O_2$ are also produced by the mechanical alloying and thermal treatment of $Fe^\circ/\alpha\text{-}Fe_2O_3$ and $Fe^\circ/\gamma\text{-}Fe_2O_3$. However, much lower activities towards $H_2O_2$ were obtained compared with $Fe^\circ/Fe_3O_4$ mixtures.

In conclusion, the results presented here point out to a special $Fe^\circ/Fe_3O_4$ interface effect which is of great significance for catalytic and especially environmental applications.

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