Mechanical Dehydration of γ-FeOOH by Wet Grinding Procedures

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The decomposition of γ-FeOOH induced mechanically in cyclohexane leads to γ-Fe_2O_3 which is more stable than the sample obtained by the thermal dehydration of unground γ-FeOOH.

In a recent communication, Klissurski and Blaskov[1] have shown that the mechanical dehydration of γ-FeOOH yields directly α-Fe_2O_3 by dry grinding in an agate mortar. This behaviour is also observed when dry grinding is carried out in a ball mill.[2] In contrast, wet grinding causes the formation of γ-Fe_2O_3.

γ-FeOOH was obtained by the method reported by Giovanoli and Brutsch.[3] The *X*-ray diffraction pattern of this sample revealed a high-purity phase. The specific surface area obtained by the Brunauer–Emmett–Teller method was $102\,m^2\,g^{-1}$. Both dry and wet mechanical treatments were performed using a planetary mill (Oliver and Batlle 20 A)

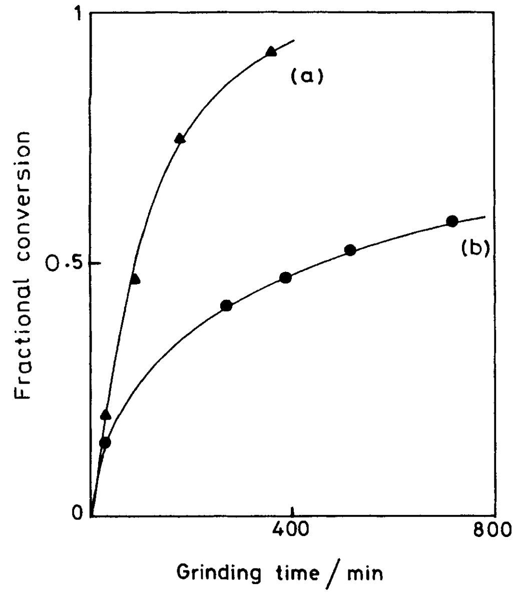

Figure 1. Relation between fractional conversion and grinding time, (a) dry milling (dehydration to α-Fe_2O_3); (b) cyclohexane medium (dehydration to γ-Fe_2O_3).

equipped with a hard porcelain jar, (250 ml capacity) containing three hard porcelain balls (20 mm diameter). Each treatment was interrupted at several intervals in order to characterize the products by *X*-ray diffraction (using Phillips PW 1060 instrument; Co-K_α radiation) and differential scanning calorimetry, D.S.C., (using a Mettler TA 3000 apparatus). The quantitative interpretation of the *X*-ray diffraction patterns to evaluate the fractional conversion was carried out by applying the auto-flushing theory of binary systems.[4]

The dry, mechanical dehydration of lepidocrocite† causes the transformation of this phase into α-Fe_2O_3, γ-Fe_2O_3 being undetected. This process is developed until lepidocrocite is totally transformed, Figure 1 (a). When grinding proceeds in a cyclohexane medium, however, α-Fe_2O_3 is not detected. Instead, the *X*-ray diffraction patterns show the presence of γ-Fe_2O_3. Moreover, the transformation of lepidocrocite into this phase is not completed on further grinding, at least for 12 h, see Figure 1 (b).

In addition, the γ-Fe_2O_3 formed by wet mechanical treatment increases in its thermal stability. In the initial sample of lepidocrocite the exothermal phase transition γ-Fe_2O_3 → α-Fe_2O_3, after dehydration, takes place in the range 370—440 °C, as shown by D.S.C., while the product obtained after 12 h grinding is still γ-Fe_2O_3 at 450 °C and D.S.C. shows that its transformation occurs between 500 and 570 °C. This behaviour might be indicative of an enhancement of the activation energy of the phase transition, as indicated by Nakatani *et al.*[5] However, these authors find an enhancement of the peak width in the differential thermal analysis curves of γ-Fe_2O_3 obtained by heating dry Fe_3O_4, ground in an agate mortar, while wet ball milling did not cause this effect.

In the light of these results, the explanations based on a limited change in the stacking of the layers in the dehydration of γ-FeOOH promoted by grinding,[2] or that this treatment is unable to activate the oxyhydroxide to yield γ-Fe_2O_3,[1] need to take into account the different media in which grinding is carried out.

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† Lepidocrocite = natural form of γ-FeOOH.

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