

## Thermogravimetric and Mössbauer investigation of the reduction of $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and Li<sub>0.5</sub>Fe<sub>2.5</sub>O<sub>4</sub>

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**Abstract.** The reduction of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and Li<sub>0.5</sub>Fe<sub>2.5</sub>O<sub>4</sub> by hydrogen has been studied to characterise the stages of reduction. The course of reduction as followed by TGA and Mössbauer spectroscopy indicates that (i) in the case of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, the reduction to metallic iron goes through the intermediate formation of Fe<sub>3</sub>O<sub>4</sub>, and (ii) in the case of Li<sub>0.5</sub>Fe<sub>2.5</sub>O<sub>4</sub> the reduction proceeds in a single step to give a mixture of LiFeO<sub>2</sub> and Fe.

**Keywords.** Thermogravimetry; Mössbauer spectroscopy; reduction process;  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>; Li<sub>0.5</sub>Fe<sub>2.5</sub>O<sub>4</sub>.

### 1. Introduction

The reduction process of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> in the solid state by hydrogen to the metallic form drew considerable attention of many investigators. There is general agreement that below 843 K the reaction could be stepwise as Fe<sup>3+</sup> → Fe<sup>2+</sup> → Fe<sup>0</sup>, but it is observed to occur as a single step (Fe<sup>3+</sup> → Fe<sup>0</sup>) due to the instability of the intermediate oxides. Further, the nature of the intermediate has also been variously reported as a spinel more oxidised than Fe<sub>3</sub>O<sub>4</sub> (Finch and Sinha 1957; Kojima 1954), as  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (Aharoni *et al* 1962) or as a phase more reduced than magnetite (Colombo *et al* 1967).

While reduction studies of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> dispersed on the so-called inert Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> (Hobson and Campbell 1967; Boudart *et al* 1975) have been made with a view to elucidate their catalytic activities, little information is available on the reduction properties of such systems as  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-Li<sub>2</sub>O. It is often important to have information regarding the oxidation states and the relative reducibility of metal ions or oxides present on the surface layer. For example, the oxidative dehydrogenation reactions proceed *via* a redox cycle involving the formation of at least one cation of a lower valency state by reaction with a reactant (say, a hydrocarbon) and its subsequent reoxidation by oxygen from the gas phase.

The present paper deals with the reduction studies of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and Li<sub>0.5</sub>Fe<sub>2.5</sub>O<sub>4</sub> by hydrogen with a view to characterise the stages of reduction using thermogravimetry and Mössbauer spectroscopy.

## 2. Experimental

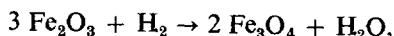
$\alpha$ -Fe<sub>2</sub>O<sub>3</sub> was obtained by calcining ferric hydroxide obtained by precipitation from a solution of ferric nitrate and ammonia at 1200 K in air. The ferric nitrate used was of AR grade. The product was subsequently identified by x-ray diffraction. For the mixed oxide system the requisite amounts of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and Li<sub>2</sub>CO<sub>3</sub> (molar ratio 5:1) were mixed intimately, pelletised, fired at 1200 K for 36 hr and furnace cooled under ordinary atmospheric conditions. The x-ray diffraction analysis of the product characterised it as inverse spinel Fe<sub>3.0</sub><sup>2+</sup> [Li<sub>0.5</sub><sup>+</sup>Fe<sub>3.5</sub><sup>1+</sup>] O<sub>4</sub><sup>2-</sup>. The thermograms were taken on a recording thermogravimetric apparatus fabricated in our laboratory using phosphor bronze spring and a linear velocity differential transducer. A platinum bucket was used as sample holder. The heating rate was maintained by manual control at 6°/min and the mass losses were recorded directly on a recording potentiometer. The sensitivity of the instrument was 50 mg for full scale (25 cm) of the recorder. The room temperature Mössbauer spectra were recorded in a spectrometer with a single channel analyser and mechanical drive using <sup>57</sup>Co/Cr and <sup>57</sup>Co/Cu source.

The reduction of the samples was carried out as follows. 200 mg of the sample was taken in a porcelain boat and placed in a quartz tube that was externally heated in a tubular furnace. The temperature of the sample was controlled within  $\pm 5$  K. The temperature of the sample was raised to the desired level in a current of UHP nitrogen (supplied by Indian Oxygen) dried by passing through phosphorous pentoxide. After reaching the desired temperature, dry hydrogen gas was introduced. After reduction, the sample was slowly cooled to room temperature in a current of dry nitrogen gas. Use of larger quantities of sample was avoided as that showed inhomogeneity between the surface and the bulk.

## 3. Results and discussion

### 3.1. Reduction of $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>

The thermogram for the reduction of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> by hydrogen showed two distinct steps (figure 1). The mass losses for the first step (3.1% with onset temperature of  $\sim 600$  K) and for the overall reduction (29.70%) could be accounted for by the following reactions:



The close agreement between the theoretical and observed mass losses led to the inference that the intermediate corresponds to the complete conversion of Fe<sub>2</sub>O<sub>3</sub> to Fe<sub>3</sub>O<sub>4</sub>.

The room temperature Mössbauer spectra of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> reduced by hydrogen at 673 K for different durations are shown in figure 2. The spectra (a) to (c) are complex indicating the presence of several phases. One of the six line patterns could be easily identified as due to metallic iron. The spectrum after subtracting

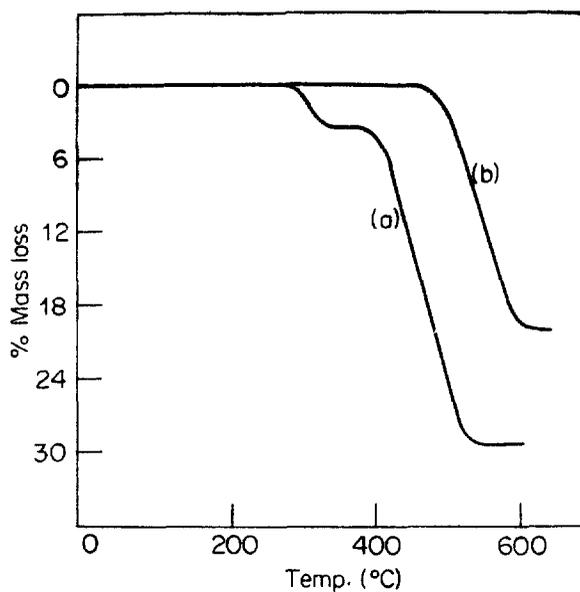


Figure 1. TGA curve for the reduction by hydrogen of (a)  $\alpha\text{-Fe}_2\text{O}_3$ , (b)  $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ .

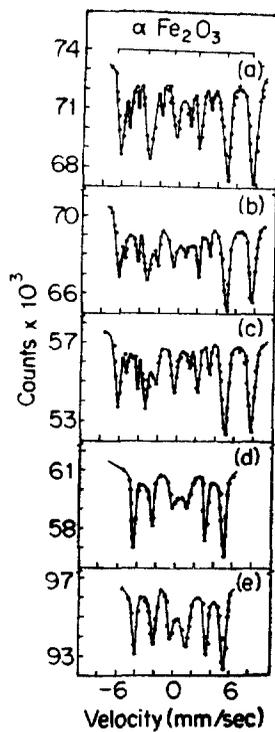


Figure 2. Mössbauer spectra of  $\alpha\text{-Fe}_2\text{O}_3$  reduced by hydrogen (a) 30 min, (b) 1 hr, (c) 1.5 hr, (d) 3 hr, (e) 4 hr.

that due to iron appeared to be a superposition of two six line patterns indicating the presence of  $\text{Fe}^{3+}$  at two lattice sites. The hyperfine field for the outermost lines was  $490 \pm 20$  K Oe and for the next to outermost lines was  $460 \pm 20$  K Oe. Comparing with the values reported for different oxides (Ron 1972), the phase could be identified as  $\text{Fe}_3\text{O}_4$ , an inverse spinel with cation distribution as  $\text{Fe}^{3+}[\text{Fe}^{3+}\text{Fe}^{2+}]\text{O}_4^{2-}$ . Formation of  $\gamma\text{-Fe}_2\text{O}_3$  was not detected by Mössbauer spectroscopy. Further, the absence of an intense central peak in the spectrum shows that FeO is absent. This is consistent with our TGA studies and also with Fe-O phase diagram (Darken and Gurry 1946) which indicates that FeO is unstable below 843 K and, if formed, disproportionates to  $\text{Fe}_3\text{O}_4$  and Fe. This disagrees with the results of Ramonov *et al* (1973) who reported the formation of the FeO phase at temperature well below its eutectic transformation temperature (843 K).

As to the nature of  $\text{Fe}_3\text{O}_4$  formed during the reduction, there is no indication as discussed below for the formation of any specific oxidised ( $\text{Fe}_{3-x}\text{O}_4$ ) or reduced ( $\text{Fe}_{3+w}\text{O}_4$ ) spinel. In stoichiometric  $\text{Fe}_3\text{O}_4$  as represented by  $\text{Fe}^{3+}[\text{Fe}^{2+}\text{Fe}^{3+}]\text{O}_4^{2-}$ , the ratio of  $I_B/I_A$  (where  $I_A$  and  $I_B$  are the integrated intensity of Mössbauer lines for the cations at  $A$  and  $B$  sites respectively) is reported to be 1.88 (Sawatzky *et al* 1969). In the case of oxidised spinel  $\text{Fe}_{3-x}\text{O}_4$ , cation vacancies are expected to occur at  $B$  sites. To preserve charge balance, a portion of  $\text{Fe}_B^{2+}$  cations will be oxidised leading to the existence of unequal  $\text{Fe}^{3+}$  in the prevalent  $\text{Fe}^{3+}-\text{O}-\text{Fe}^{2+}$  couple. In such a case, the excess  $\text{Fe}_B^{3+}$  ions not coupled with  $\text{Fe}_B^{2+}$  will not be taking part in the fast electronic exchange, and hence would give rise to their own six-fingered pattern which will overlap with that of  $A$  site  $\text{Fe}^{3+}$ . On the other hand, in reduced magnetite there will be excess of  $\text{Fe}^{2+}$  at  $B$  sites not taking part in the fast electronic exchange, and thus will produce its own six line pattern.

Assuming that the recoil free fraction is the same for both  $A$  and  $B$  sites and that the ratio ( $I_{B'}/I_{A'}$ ) of the intensities of the outermost lines on the negative velocity side is equal to  $I_B/I_A$ , the area under the lines  $A'$  and  $B'$  were calculated. The ratio was found to be 1.65. This is substantially higher than the value 1.06 reported for  $\text{Fe}_{2.91}\text{O}_4$  (Coey *et al* 1971). Although our value (1.65) is lower than that reported for stoichiometric  $\text{Fe}_3\text{O}_4$  (1.88), it is still in much better agreement with  $\text{Fe}_3\text{O}_4$  than with  $\text{Fe}_{2.91}\text{O}_4$ . The slightly lower value in our case may be due to the fact that our calculations were based on the splitting of only one line in the room temperature spectrum, whereas Sawatzky *et al* (1969) obtained the value 1.88 in a completely resolved spectrum obtained at low temperature in the presence of external magnetic field. Similarly, the absence of extra six line pattern due to  $\text{Fe}^{2+}$  excludes the possibility of reduced spinel. Deviation from the stoichiometry  $\text{Fe}_3\text{O}_4$ , if any, is not within detectable limit. The spectra (d) and (e) are simple six-fingered patterns and could be identified as metallic iron from the Mössbauer parameters.

### 3.2. Reduction of $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$

The thermogram for the reduction of  $\text{Fe}^{3+}[\text{Li}_{0.5}^{2+}\text{Fe}_{1.5}^{3+}]\text{O}_4^{2-}$  by hydrogen (figure 1) indicated a single step process in contrast to the two-step process in  $\alpha\text{-Fe}_2\text{O}_3$ . Further, the onset of reduction was around 770 K in contrast to 600 K for  $\alpha\text{-Fe}_2\text{O}_3$ . The mass loss (21.70%) computed from the thermogram showed a large deviation from the theoretical mass loss (28.92%) corresponding to the formation of Fe

and  $\text{Li}_2\text{O}$ . It is apparent that all the iron species ( $\text{Fe}^{3+}$ ) in the starting material are not completely converted to metallic iron under the prevailing conditions.

The room temperature Mössbauer spectra of the reduced samples (figure 3) consisted of a magnetically split component superposed by an intense central peak when compared to the simple six line pattern for the unreduced sample. Five of the six magnetically split components were visible with the sixth peak (i.e. first peak on the positive side) hidden in the central region of the spectrum. The magnetically split component could be identified as due to metallic iron from the Mössbauer parameters (isomer shift = 0 with reference to Fe and  $H_{\text{eff}} = 330 \text{ KOe}$ ). A computer analysis of the central peak led to a doublet with I.S. of  $+0.47 \text{ mm/sec}$  with respect to iron and quadrupole splitting of  $0.52 \pm 0.07 \text{ mm/sec}$ . With increase in duration of reduction the line positions remained unaltered, but the intensity of the central peak decreased relative to those of magnetically split components. It was not possible to effect further reduction even by prolonging the reduction time to 10 hr as indicated by the spectra as well as by the mass loss data.

The following reactions could be proposed for the reduction process:

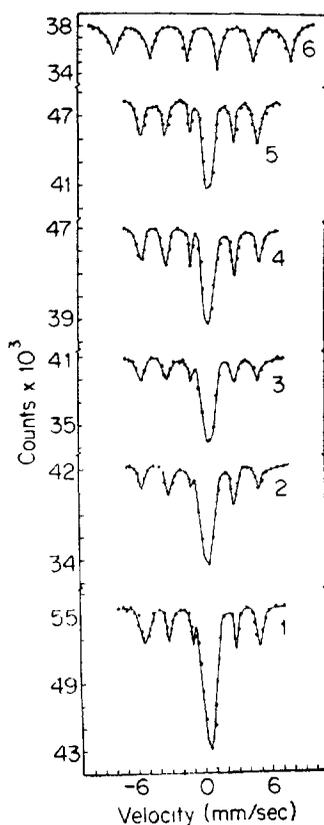
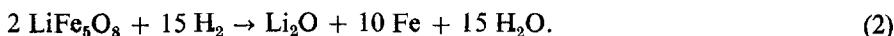
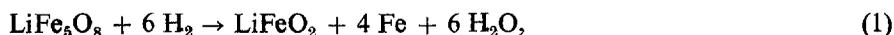


Figure 3. Mössbauer spectra of reduced samples of  $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ , (1) 2 hr, (2) 2.5 hr, (3) 3 hr, (4) 4 hr, (5) 7 hr, (6) reoxidised.

The theoretical mass losses were calculated for the above two reactions. Reaction (1) gave 23.17% and (2) gave 28.92% mass loss. The observed mass loss of 21.70% excludes the possibility of reaction (2). As mentioned earlier, the presence of quadrupole split at the centre of the spectrum also supported the above argument, since the only iron species in reaction (2) is metallic iron.

On the other hand, if the reaction (1) occurred,  $\text{LiFeO}_2$  would give rise to its characteristic spectrum consisting of central doublet (I.S. = 0.37 and Q.S. = 0.55 mm/sec) (Cox *et al* 1963). The close agreement between the reported Mössbauer parameters of  $\text{LiFeO}_2$  and spectrum of the reduced sample led us to identify the second phase as  $\text{LiFeO}_2$ . Besides, the x-ray diffraction patterns of the reduced sample showed the most intense lines of  $\text{LiFeO}_2$  besides those due to metallic iron.

The spectrum of the reoxidised sample consisted of a six-line pattern and from the line positions, the phase could be identified as  $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$  thereby establishing that the original structure is regenerated.

#### 4. Conclusions

From TGA and Mössbauer studies, it appears that the reduction of  $\alpha\text{-Fe}_2\text{O}_3$  by hydrogen under the given conditions is identified with a distinct two-step process with the intermediate  $\text{Fe}_3\text{O}_4$ . In the  $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$  system under the given conditions of reduction by hydrogen, part of the iron species goes to metallic state and the remaining remains as  $\text{LiFeO}_2$ .

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