

TABLE 4

TOTAL H₂O AND ADSORBED H₂O OF γ -FeOOH

| | Preparation No. | | | |
|---|-----------------|------|------|------|
| | 1 | 2 | 3 | 4 |
| Found % | 12.7 | 12.5 | 16.7 | 16.6 |
| Difference to 10,14% (theoretical) in % | 2.6 | 2.4 | 6.6 | 6.5 |

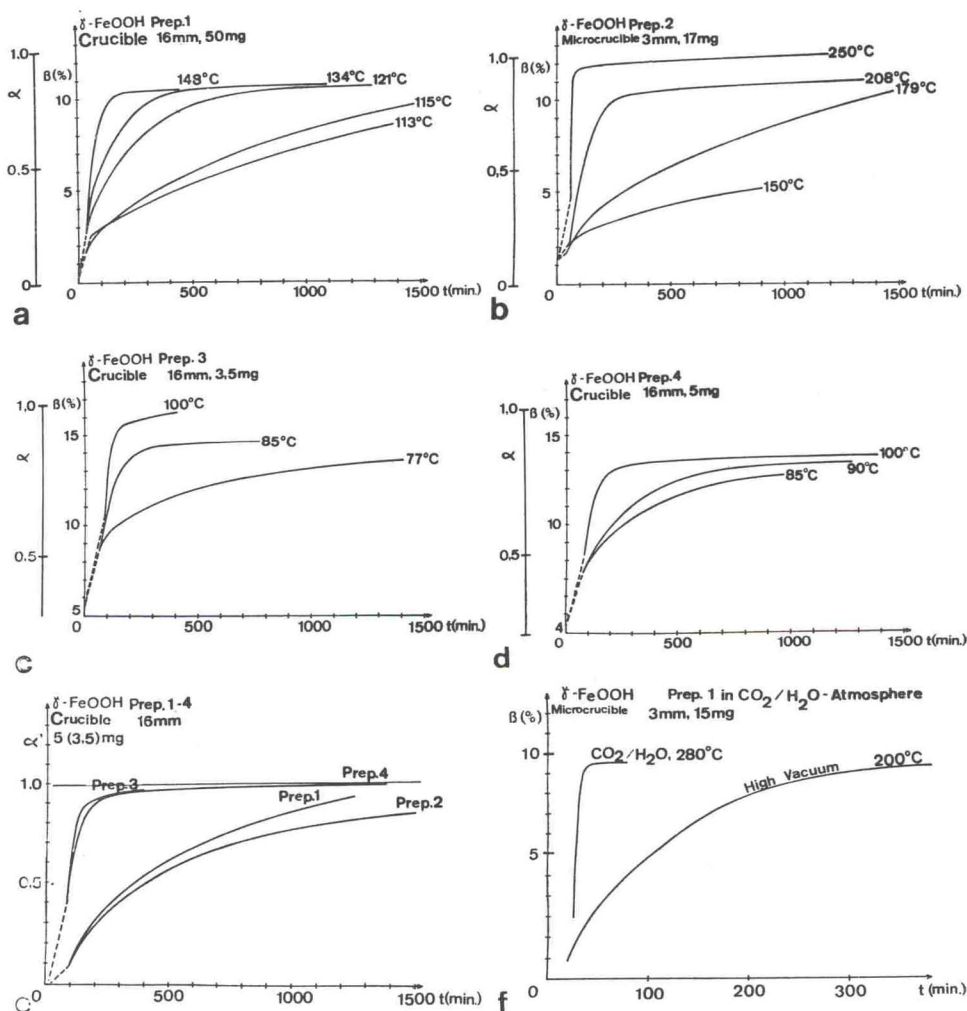


Fig. 3 Isothermal decomposition at various temperatures. (a) Preparation 1 decomposed in vacuo. (b) Preparation 2 decomposed in vacuo. (c) Preparation 3 decomposed in vacuo. (d) Preparation 4 decomposed in vacuo. (e) Influence of crystallite size on decomposition at 100°C in vacuo. (f) Influence of atmosphere (water vapour pressure) on isothermal decomposition of preparation 1.

2. Isothermal decomposition

2.1 Decomposition in vacuo. Decomposition curves in vacuo of samples No. 1-4 are of similar shape. The reaction starts very fast, slows down within about 0.5-5 h (after having reached isothermal conditions) and ends sluggishly (Fig. 3). It should be noted, however, that no one set is actually identical to any of the others. In some instances, whole sets have been repeated to get more data. The measurements could be improved (in reproducibility) with larger samples; under such conditions, however, the decomposition water is not removed fast enough even under 10^{-5} torr, and a water vapour pressure builds up thus increasing the reaction rate as will be shown later. This being most undesirable, we were forced to accept the compromise of smaller samples and poorer reproducibility. The sample thickness could not be brought below 0.5 mm*.

As we shall see from x-ray evidence a H_2O atmosphere increases the reaction rate. Nevertheless Fig. 3b which represents a compressed sample shows a decrease in the reaction rate. The explanation is that in fact the reaction is faster but the desorption of the water is much slower, the balance pan then erroneously giving too high a sample weight (including H_2O) thus leading to the false conclusion of a slower reaction while it is actually enhanced.

This, like some other phenomena, underlines the importance of checking TG results by independent measurements.

As expected sample 3 with the smallest crystallite size (highest specific surface) decomposes faster than all three others, as can be seen from Fig. 3e which shows the TG curves at 100°C for all four samples. α' is the decomposed fraction:

$$\alpha'(t) = \frac{y(t) - x}{y_0 - x}$$

where: $y(t)$ = weight loss after time t ; x = weight loss during evacuation; y_0 = weight loss attained at constant weight.

2.2 Decomposition in H_2O atmosphere. A set of isothermal decomposition curves under water vapour would have been desirable; but for reasons of time, only one run at 280°C could be undertaken and may be shown together with a vacuum experiment at 200°C (Fig. 3f). p_{H_2O} was 646 torr; the carrier gas was CO_2 . Although the two curves in Fig. 3f are not directly comparable, it is obvious that H_2O enhances the decomposition. This is backed by x-ray evidence. The x-ray identification of the end product of Fig. 3f proves that not only is the reaction faster but also $\alpha-Fe_2O_3$ has nucleated (Fig. 4).

3. Reduced time plots

Results as shown above in real time may be approximated by least square methods to a very high degree of accuracy. This is, in our view, misleading, as such

*The layer thickness in Fig. 8 is a calculated value from sample weight and crucible diameter and may therefore be below 0.5 mm.