

THERMAL DECOMPOSITION OF IRON SULPHATES

I. THERMOGRAVIMETRIC STUDY OF $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ IN CARBON MONOXIDE AND HYDROGEN ATMOSPHERES

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ABSTRACT

Thermal decomposition of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ in carbon monoxide has been studied up to 900°C by thermoanalytical methods and the reaction products and intermediates identified by Mössbauer, IR and X-ray diffraction techniques. The main reaction products are elemental iron and ferrous sulphide; at higher temperatures, cementite is formed as well. For comparison, experiments have also been carried out in hydrogen atmosphere.

INTRODUCTION

Considerable interest has been focused on the use and disposal of ferrous sulphate, which is a by-product produced in excess of demand in several industrial processes, e.g., sulphuric acid pickling of steel, smelter slag leaching and titanium dioxide production.

If economically feasible, thermal decomposition could be a useful way of converting ferrous sulphate and its various hydrates into more valuable products and raw materials. This has been the subject of several recent studies, most of them done in oxidizing or inert atmospheres^{1–7}. Only a few investigations have so far been undertaken in reducing atmosphere; of these, the studies by Pannetier and Bugli in hydrogen atmosphere are the most comprehensive^{8–9}.

The aim of the present investigation was to establish by thermoanalytical methods the decomposition route of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ in carbon monoxide. For comparison, similar experiments were also carried out in hydrogen atmosphere. The reaction intermediates and final products were identified by X-ray diffraction, and Mössbauer and IR spectrometry.

EXPERIMENTAL

Ferrous sulphate monohydrate was prepared by recrystallizing $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, an analytical grade reagent from Noury-Baker N.V., from a hot sulphuric acid

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solution. The precipitate was washed with ethanol and ether and its composition was confirmed by chemical analysis and X-ray diffraction.

TG, DTG and DTA curves in dynamic (5 l h^{-1}) carbon monoxide (99.9%) and hydrogen atmospheres were recorded simultaneously with a Mettler thermoanalyzer. The heating rates in CO-atmosphere were 1°C min^{-1} and 6°C min^{-1} and in H_2 -atmosphere 6°C min^{-1} . Standard Mettler platinum crucibles (diam. 7 mm, depth 19 mm) were employed. In DTA measurements alumina was used as reference material.

In addition to thermoanalyzer experiments, larger samples (500 mg) were heated isothermally in a quartz vessel (50 cm^3) with a gas flow-rate of 5 l h^{-1} . The temperature range investigated in these batch experiments was $250\text{--}900^\circ\text{C}$.

For Mössbauer measurements the samples were taken from the batch experiments and quenched in CO-atmosphere to room temperature. ^{57}Co in Cu was used as source and absolute calibration of the velocity scale was achieved with a laser. Measurements were carried out at room temperature. The source was moved relative to the absorber with a constant acceleration drive. The spectra were recorded on an 800-channel analyzer.

X-ray diffraction patterns were recorded with a Philips powder diffractometer using Ni-filtered CuK_α radiation. IR spectra were measured on a Perkin-Elmer 521 instrument using the KBr pellet technique.

RESULTS AND DISCUSSION

The results of thermoanalyzer and batch experiments in carbon monoxide are summarized in Fig. 1 which gives the observed weight loss as a function of temperature.

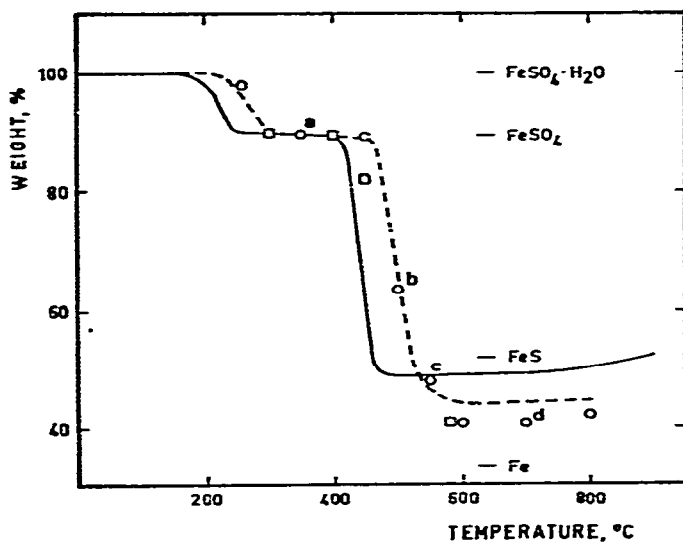


Fig. 1. Thermal decomposition of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ in carbon monoxide. Heating rate and sample weight: (—) 1°C min^{-1} and 70.7 mg; (---) 6°C min^{-1} and 72.0 mg. The symbols refer to isothermal experiments [(O) 1 h; (□) 2 h] and the small letters to Mössbauer measurements of Fig. 3.

The initial step in the decomposition and reduction reactions is the dehydration



When a heating rate of 1°C min^{-1} is employed, this reaction begins at 150°C and is completed at 260°C ; the higher heating rate of 6°C min^{-1} causes the dehydration to begin and end at temperatures approximately 50°C higher. At this stage the batch experiments with 1 h heating time correspond generally to the faster heating rate, and those with the 2 h reaction time to the 1°C min^{-1} TG curve.

The dehydration product in all experiments was found by X-ray diffraction to be $\alpha\text{-FeSO}_4$ (ref. 10). The IR spectrum for a sample taken from the plateau corresponding to anhydrous FeSO_4 showed no absorption maxima in the OH-stretching region, thus excluding the presence of FeOHSO_4 found in experiments performed in air and oxygen^{1,2,4,7}. The Mössbauer spectrum for a sample quenched from this plateau (cf. Fig. 3a) was consistent with X-ray diffraction and IR results. It showed only a doublet with a quadrupole splitting $\Delta E = 3.10 \pm 0.03 \text{ mm sec}^{-1}$, and an isomer shift relative to iron $\delta = 1.29 \pm 0.03 \text{ mm sec}^{-1}$. The values reported in the literature for quadrupole splitting of FeSO_4 are somewhat lower^{2,6,7,11}; this might be because different polymorphs were investigated.

The second step involves a much greater weight loss of approximately 50% owing mainly to the reduction of FeSO_4 to FeS and Fe . The TG and DTG curves indicated the reduction to proceed smoothly in a single step, but according to the DTA curve (Fig. 2) the exothermic reaction is a two-stage process.

X-ray diffraction patterns indicated that disproportionation occurs too, especially at temperatures under and around 500°C . The X-ray patterns showed the presence of ferric iron as Fe_3O_4 in samples taken at 500°C . In agreement with this, the Mössbauer

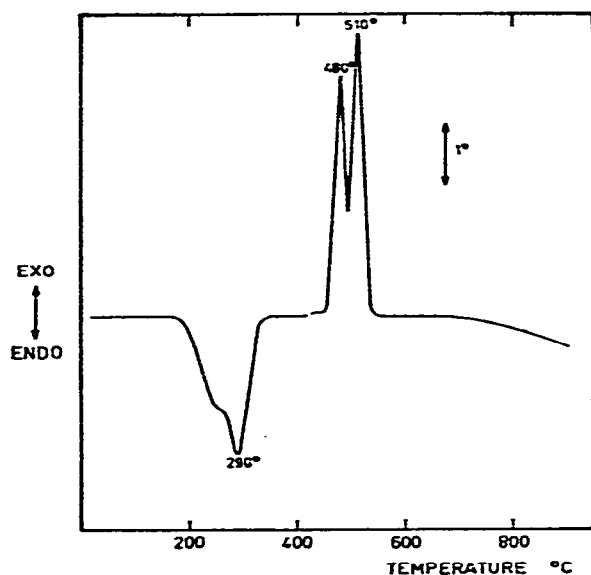


Fig. 2. DTA curve for decomposition in CO , heating rate 6°C min^{-1} . Sample weight 72.0 mg.

spectrum for the same sample (Fig. 3b) showed, in addition to the FeSO_4 doublet, a complex set of lines which can be attributed to Fe_3O_4 . Although the spectrum is somewhat diffuse, the magnetic field values obtained (480 and 445 kG) agree with the values reported previously for the two Fe sites in magnetite¹².

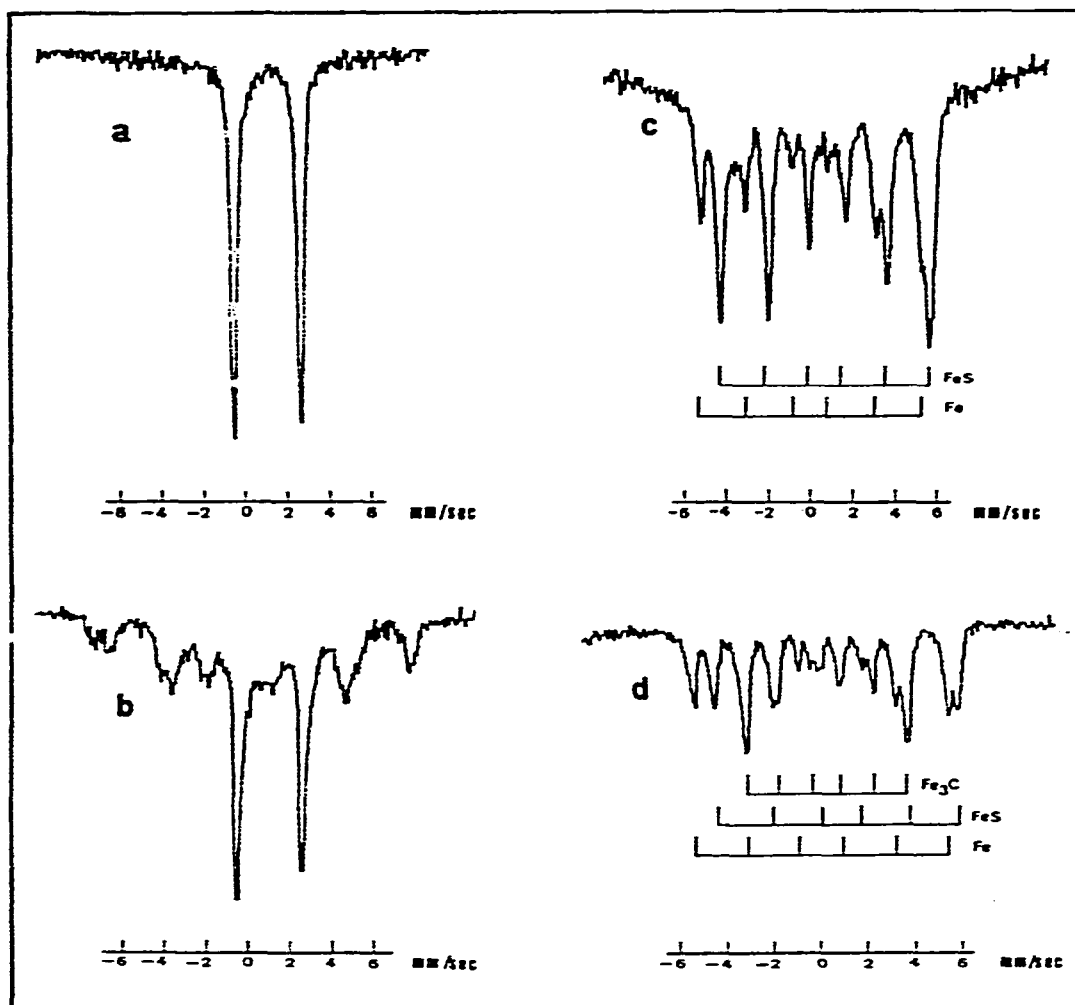


Fig. 3. Mössbauer spectra of samples quenched in CO to room temperature after 1 h heating at: (a) 350 °C; (b) 500 °C; (c) 550 °C; and (d) 700 °C.

Constant weight is achieved above 500 °C at a level which corresponds to reduction beyond FeS. The presence of elemental iron at 550 °C as a major reaction product was clearly visible in both X-ray diffraction patterns and the Mössbauer spectrum (Fig. 3c). From the intensities of the overlapping Mössbauer spectra it can be concluded that the sample at this stage contains only a negligible amount of FeSO_4 in addition to the major components FeS and α -Fe. The magnetic field values found for FeS and Fe were 310 and 330 kG, respectively.

When thermal analysis is continued above 700°C the weight of the sample is observed to increase slightly. A plausible explanation for this phenomenon is the deposition of carbon on the sample due to decomposition of carbon monoxide:



It is known that elemental iron catalyzes this decomposition reaction¹³. The carbon may then react with the iron and form cementite and indeed, the diffraction patterns of samples reduced at higher temperatures showed the presence of Fe₃C. The Mössbauer spectrum confirmed the presence of Fe₃C (H = 210 kG) as the major reaction product at 700°C, together with Fe and FeS, cf. Fig. 4d. The effect of deposited carbon on the sample weight is more pronounced in thermobalance experiments where the sample weight is relatively small than in the batch experiments.

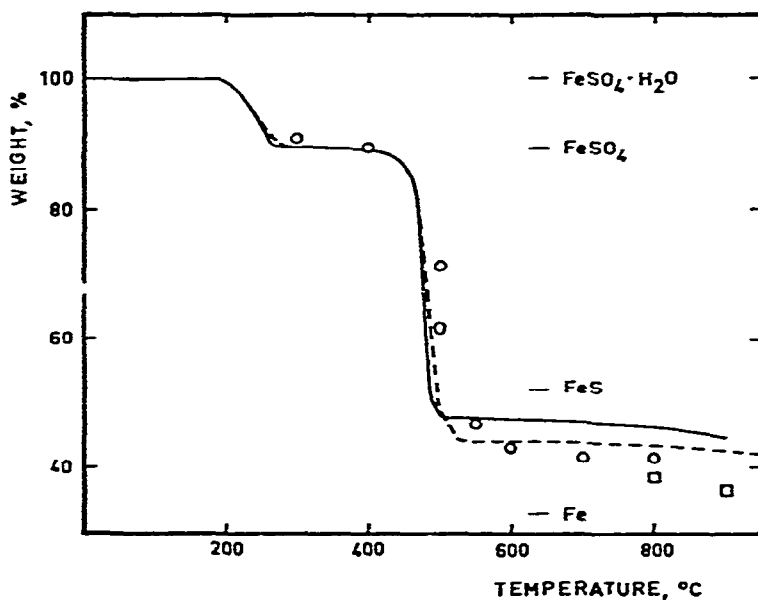


Fig. 4. Thermal decomposition of FeSO₄·H₂O in hydrogen. Heating rate is 6°C min⁻¹ and sample size (—) 67.5 mg (---) 149.7 mg. Symbols for isothermal experiments are as in Fig. 1.

For comparison, similar experiments were also carried out in hydrogen atmosphere and the results are summarized in Fig. 4. There are small differences in the reaction temperatures but generally the reactions proceed in a similar manner as in carbon monoxide atmosphere. The present results in hydrogen are in good agreement with those obtained by Pannetier and Bugli^{8,9}.

In both atmospheres the batch experiments showed a greater overall weight loss than the thermogravimetric experiments. This is probably due to the loss of sulphur dioxide during the main reduction step around 500°C when fast heating is employed⁹. The sample weight has also a little effect on the results. (Cf. Fig. 4).

The main difference between the two reducing media seems to be the absence of

a weight minimum in the TG curve obtained in H_2 . Rather, the reduction in H_2 proceeds more completely towards elemental iron as the temperature increases. This supports the explanation given above for the observed weight increase in carbon monoxide atmosphere above $700^\circ C$.

It can be concluded that the thermal decomposition of ferrous sulphate in carbon monoxide is a complex process involving several reaction intermediates. In addition to the reduction by carbon monoxide, several competing solid state reactions may occur, as shown to proceed when reduction is carried out in hydrogen⁹. Further work aimed at clarifying the kinetic aspects of the reduction is in progress.

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