MOSSBAUER STUDIES OF THE THERMAL DECOMPOSITION OF
IRON(II) AMMONIUM SULPHATE HEXAHYDRATE

E. FRANK, M. C. VARRIALE and A. BRISTOTI

Instituto de Física, Universidade Federal do Rio Grande do Sul; * Instituto de Física and Programa de Pós-Graduação em Engenharia Metalúrgica e dos Materiais, Universidade Federal do Rio Grande do Sul, 90000 Porto Alegre, Brasil

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The thermal decomposition products of Mohr's salt, \((\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}\), in static air have been studied in the temperature range 25—800°C. Mössbauer spectroscopy, X-ray diffractometry and thermal analysis were used in the identification of the intermediates. \(\text{Fe}^{2+}\) compounds containing 4, 2 and zero \(\text{H}_2\text{O}\) were identified and the possibility of occurrence of \((\text{NH}_4)_2\text{Fe}_2(\text{SO}_4)_3\) is advanced. The presence of \(\text{Fe}^{3+}\) was detected starting at 230°C for a 1.67°C/min heating rate, and the compounds \((\text{NH}_4)\text{Fe}(\text{SO}_4)_2\) and \(\text{Fe}_2(\text{SO}_4)_3\) were also identified.

Mohr’s salt, iron(II) ammonium sulphate hexahydrate, \((\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}\) (hereafter HHFAS), belongs to the monoclinic crystal system, space group \(P 2_1/\alpha\), with unit-cell dimensions \(a = 9.32\) Å, \(b = 12.65\) Å and \(c = 6.24\) Å and \(\beta = 106.8°\) [1]. Its thermal decomposition products have been studied by several authors [2—4]. The results were vague and not absolutely conclusive. Whereas Pascal indicates a loss of water and some ammonia from 100°C onwards, and the formation at 290°C of the anhydrous alum \((\text{NH}_4)_\text{Fe}(\text{SO}_4)_2\), Wendlandt indicates the range from 192 to 310°C extending up to 450°C.

The present work describes the identification of the thermal decomposition products of HHFAS under non-isothermal conditions and combines the capabilities of thermal analysis [5] and Mössbauer spectroscopy [6].

As only small changes were to be expected between some of the decomposition products of HHFAS, it was felt that Mössbauer spectroscopy, with its unique capability of detecting small variations in the coordination sphere of iron atoms, was extremely suitable for this purpose.

The aim of the present study is to give as detailed as possible an account of the development of the thermal decomposition of HHFAS and to determine the temperature of passage from \(\text{Fe}^{2+}\) to \(\text{Fe}^{3+}\). No gas analysis was performed and X-ray identification at room temperature was performed only for the less hygroscopic products.

Experimental

The samples used were Merck reagent grade (natural unenriched iron) HHFAS and were heated in static air in a derivatograph manufactured by MOM (Budapest), model 1969. This equipment gives simultaneously the mass loss curve (TG),

+ Present address: Quimica Hoechst S. A., Corrientes 222, Argentina

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the derivative of the mass loss (DTG) and the DTA curve. It also gives the temperature \(T\) inside the sample. The heating system can be stopped at any temperature of interest, due to the fact that all four curves can be followed simultaneously by visual inspection. By this procedure the beginning, the maximum rate and the end of the chemical reaction due to the heating process can be determined, and a quenching method can be attempted in order to isolate different compounds or phases. The minima of the DTA curve \(T\) and some intermediate points were used in the present study to prepare the products of thermal decomposition of HHFAS, by quenching each one to room temperature. Several heating rates were tried in order to study all the details of the thermal decomposition process without loss of information: 1.6°/min was chosen. Each sample (1 g HHFAS) was heated to the desired temperature, and removed from the oven to a glove-bag filled with commercial Ar, where the encapsulation was performed. Typical times required to transfer the samples from the oven to the bag, and to encapsulate them, were 5 and 15 min, respectively. “O” ring sealed absorber holders were used, with an effective area of 2.5 cm². Mössbauer spectra were run with around 30 to 40% of the total sample after mixing the several layers of different shapes and compactness which could be detected in the crucible taken from the oven. This led to somewhat thick Mössbauer samples (up to a maximum total iron content of 25 mg/cm²). Tightly of the absorber holders was checked by running the spectra of several samples over a period of 3 weeks, with no appreciable change of the relative intensity of the components of the mixture, whereas opening of the absorber holders for a few minutes (and subsequent reclosing) introduced a noticeable change. Therefore, any possible rehydration of the samples must have occurred in the period of the quenching process and sample encapsulation in a water-poor atmosphere.

A constant acceleration Mössbauer effect spectrometer built around a PDP 11/10 computer, together with a NaI(Tl) scintillation counter and a conventional amplifying line, were used. The software was programmed so as to obtain a triangular velocity wave form and the accumulation was performed on separate halves (256 channels each) of the computer memory for the increasing and the decreasing velocities, respectively. Deviations from linearity are less than 0.5% over some 95% of the wave form. Deviations from reproducibility over a 45-day period are better than 1%, as shown with frequent calibrations with sodium nitroprusside (SNP), which is also used as reference material for the isomer shifts (IS). A room-temperature \(^{57}\)Co in Rh source, of approximately 15 mCi strength, purchased from NENC, was used.

A standard least squares fitting procedure, using independent lorentzian lines, was performed on each half of the spectra. The reported values are the means of the values for the two halves, which never differed by more than the above mentioned linearity limit.

The more complex spectra (230° and 260°) were analyzed using a stripping method which we have previously reported \([8]\). Both methods were used on a HP-2100 A computer with a 16K bite memory.

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