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Thermal dehydration and decomposition of copper selenate pentahydrate

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Abstract Temperature programmed desorption mass spectrometry (TPD-MS) and thermal gravimetry (TG) were utilized for the study of the thermal dehydration and decomposition of copper selenate pentahydrate ($CuSeO_4 \cdot 5H_2O$). From the two techniques we suggest that the dehydration is a 3-step process reaching completion at 300 °C. The decomposition process however, is far more complicated consisting of several successive steps occurring between 480 and 900 °C. Initiated with the emission of oxygen, the decomposition of the anhydrous salt continues with SeO_2 emission via several unstable intermediates up to the conversion of the remaining copper monoxide into dicopper monoxide accompanied by oxygen emission.

Keywords Copper selenate · MS · TG · Thermal decomposition · Thermal dehydration · TPD

Introduction

The thermal dehydration and decomposition routes of metal sulfate hydrates, and in particular of copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$), are well established in the literature [1–3]. Nonetheless, studies on selenate hydrates are by far less common. Copper selenate pentahydrate is the corresponding isomorphic form of copper sulfate pentahydrate. Despite of being isomorphic forms, the thermal behavior of the selenate pentahydrate seems to differ profoundly in complexity and sensitivity to experimental conditions. This complexity is well emphasized by discrepancies in the values published for its dehydration completion temperature. While Gospodinov et al. [4] found that the dehydration comes to completion at 270 °C, Nabar et al. [5] claimed for a 500 °C value whereas Koleva et al. [6] obtained the anhydrous salt already at a temperature as low as 220 °C. Not only that these studies contain discrepancies with respect to the number of dehydration steps and stoichiometry of desorbed water molecules per step, they also diverge from the known copper sulfate dehydration route.

Nabar et al. also studied the later on decomposition of several divalent metal [5] as well as some rare-earth [7] selenates. They concluded that most of the anhydrous selenates are first reduced to selenites. Upon further heating the selenites are converted into oxides with SeO_2 emission. Of all selenates examined, $CuSeO_4$ showed exceptional behavior, suggesting a different decomposition route: first, basic copper selenate ($CuO \cdot CuSeO_4$) is formed, accompanied by SeO_3 emission. In a second step, SeO_3 is emitted to give the resultant oxide form.

The differences observed in the literature data for the decomposition steps and temperature may be due to the experimental conditions such as the heating rate and the water vapor.

In the present work TG and TPD-MS measurements are used to study the thermal dehydration and decomposition of copper selenate pentahydrate under inert atmosphere. Combining these techniques allowed quantitative determination of the total mass loss as well as a simultaneous qualitative composition analysis of the desorbed products

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emitted during the decomposition process. In turn, peaks assignment is more readily provided and the decomposition mechanism is determined with a higher degree of confidence.

Experimental

Pure (99.5%) $CuSeO_4·5H_2O$ (Alfa Aesar) was recrystallized by slow evaporation from aqueous solution of copper selenate at room temperature.

The salt obtained was characterized by X-ray diffraction provided with Bragg-Breutano diffractometer and using a Cu anode. The K_α line was filtered using a graphite moderator. The grown crystals were identified as >99% $CuSeO_4·5H_2O$, while the remaining <1% portion was $CuSeO_3·2H_2O$.

TPD measurements were carried out utilizing a TPD-MS apparatus [8] specially designed to work on samples under atmospheric pressure conditions. This unique device, equipped with a heated supersonic molecular beam inlet, enables quantitative measurement of water emitted from the sample with a time constant of ca. 1 s. Samples were situated inside a quartz holder enclosed by a concentric cylindrical furnace. 1.5 bar helium carrier gas flowing at a rate of 40 cc/min was used. The carrier gas with the decomposition gas products expand through the nozzle into the first vacuum chamber and then to a second vacuum chamber through a skimmer. The quadruple mass spectrometer (Balzers QMG 422) is located in the second, high vacuum, chamber axially to supersonic beam. This enables that the sample flies through the mass spectrometer ion beam, free of any collisions with the walls. Sample size ranged between 300 and 1,000 μg. The samples were linearly heated (10 °C/min) from 25 to *ca.* 1,000 °C (measured at the gap between the outer face of the sample holder and the inner face of the furnace). The amount of gases evolved at each dissociation reaction was determined by integrating the area occupied by the TPD curve along the characteristic temperature decomposition range of interest. Sensitivity to water was calibrated using weighted amount of copper sulfate pentahydrate.

TG measurements were carried out on a Mettler TG\SDTA 851^e, using 70 μL crucible volume alumina crucibles, under 40 cc/min Argon flow. Sample sizes were 10–50 mg. The samples were heated at a linear rate of 10 °C/min between 25 and 950 °C, measured under the crucible holder in the sample chamber.

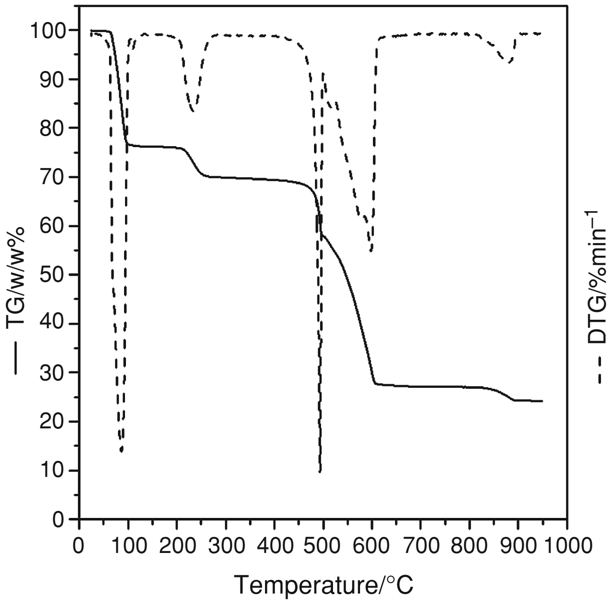

Fig. 1 TG (*continuous*) and DTG (*dotted*) curves for the thermal dehydration and decomposition of $CuSeO_4·5H_2O$ heated between room temperature and 950 °C at a linear temperature ramp of 10 °C/min

Results and discussion

TG

TG and DTG curves of $CuSeO_4·5H_2O$ dehydration and decomposition are shown in Fig. 1. Two dehydration steps are observed at 80 and 240 °C. The deeps correspond to dehydration of four and one water molecules respectively. The dehydration deep at 80 °C exhibits a shoulder at ca. 65 °C, suggesting the occurrence of total of three dehydration steps, two of which are unresolved around 80 °C.

The approximately measured weight losses in the observed dehydration steps are 23.7 and 6.3 w/o respectively, in nice agreement with the theoretical expected values of 24.3 and 6.1 w/o. The above result is in general accordance with reference [4], though our experiment seems to yield lower resolution than that obtained in Ref 4 where the first step is shown to be composed of two partially resolved dehydration peaks along the 30–100 °C temperature range rather than a sole 80 °C shouldered peak.

At higher temperatures, between 450 and 650 °C, a 2-step decomposition process of the anhydrous salt takes place. Initiated with a $½O_2$ emission between 450 and 520 °C, the decomposition proceeds via several unstable intermediates occurring between 520 and 620 °C with SeO_2 emission. The measured overall weight loss ($SeO_2 + ½O_2$) between 450 and 620 °C was 42.9 w/o which nicely agrees with 42.8 w/o, the theoretical value for SeO_3 weight loss. Finally, the decomposition is completed between 820 and 900 °C where the remaining copper monoxide is converted into dicopper monoxide with ¼O_2 emission. The measured weight loss of this final step was 2.8 w/o, again coinciding with the expected theoretical value of 2.7 w/o. Further analysis of the initiation of the anhydrous salt decomposition required a specific gas analysis of the emitted decomposition products, and is hereby discussed in the TPD section.

TPD

The TPD curve of water (m/e = 18) from $CuSeO_4{\cdot}5H_2O$ is shown in Fig. 2. Figure 2 depicts a noticeable higher resolution than that of the TG. Nonetheless, the overall TG and TPD results are in good agreement. One may note an apparent temperature shift of ca. 35 °C between the two methods. This difference may be attributed to the fact the temperature in the TPD-MS setup is sampled at the outer wall of the sample holder. Therefore, the actual temperatures are those of the TG measurements. Nonetheless, in the following discussion we present the original shifted TPD temperatures.

The high resolution of the TPD-MS measurement clearly shows that the dehydration of $CuSeO_4{\cdot}5H_2O$ is composed of three steps. By utilizing a calibration procedure, the above three desorption peaks may be respectively attributed to the emissions of 3½, ½ and 1. This result suggests the following dehydration scheme:

$$CuSeO_4 \cdot 5H_2O \rightarrow CuSeO_4 \cdot 1\tfrac{1}{2}H_2O + 3\tfrac{1}{2}H_2O\ (110\ ^\circ C)$$

$$CuSeO_4 \cdot 1\tfrac{1}{2}H_2O \rightarrow CuSeO_4 \cdot H_2O + \tfrac{1}{2}H_2O\ (130\ ^\circ C)$$

$$CuSeO_4 \cdot H_2O \rightarrow CuSeO_4 + H_2O\ (275\ ^\circ C)$$

The structure of the above scheme agrees with that suggested by Gospodinov [4], however it disagrees with the stoichiometry of released water molecules. Moreover, although our experiment nicely resolves the first two dehydration steps, we could not reconstruct the observation of Koleva [6], where the dehydration of the fifth water molecule was claimed to be formed via intermediate $CuSeO_4{\cdot}0.5H_2O$. In that respect, it is worthwhile mentioning that in several crystals we could not resolve the first two water desorption peaks. This might be attributed to a possible occurrence of a time dependent polymorphic transition of the water of crystallization molecules, as was previously observed for the analogous $CuSO_4{\cdot}5H_2O$ [9].

Further temperature elevation causes decomposition of the dried compound, a process which according to literature is accompanied by emission of SeO_2 or SeO_3, as well as O_2. Nonetheless, despite all our efforts we could not detect any SeO_2 or SeO_3 signals in the TPD-MS. SeO_2 gas, if indeed emitted from the sample, probably recondensates along the transfer line, which in our setup is constantly heated to 120 °C. Taking into account that SeO_2 sublimation temperature is 315 °C, this assumption seems probable. SeO_3 might decompose into SeO_2 and oxygen in the transfer line before reaching the mass spectrometer. Still, we could only detect the oxygen signal. The O_2 emission curve is given in Fig. 3.

Since we do not posses a calibration compound for oxygen, we can only refer to the relative peaks areas in the TPD spectrum. However, it is fair enough to assume the peak at 950 °C corresponds to ¼O_2, in accordance with the TG experiment's peak at 900 °C. The area of the sharp

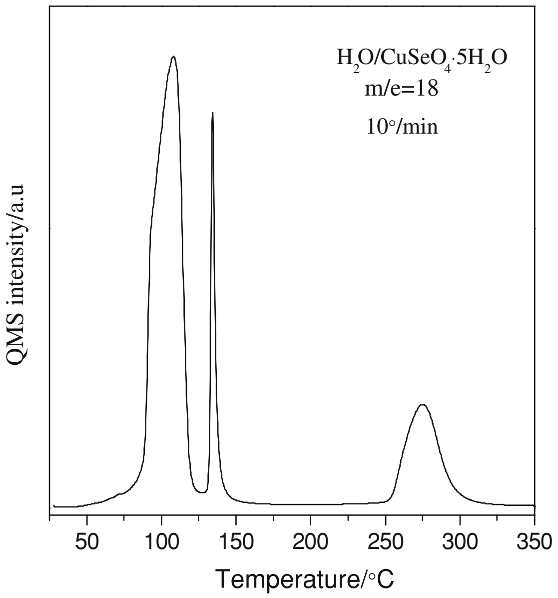

Fig. 2 TPD of water from $CuSeO_4{\cdot}5H_2O$ heated between room temperature and 350 °C at a linear temperature ramp of 10 °C/min

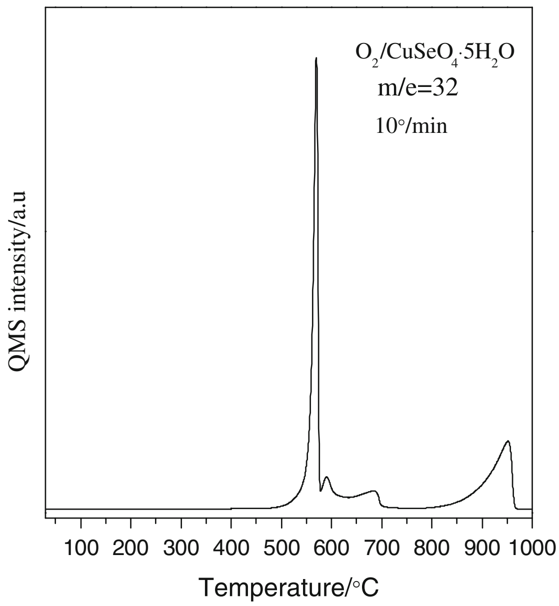

Fig. 3 TPD of oxygen from $CuSeO_4{\cdot}5H_2O$ heated between room temperature and 1,000 °C at a linear temperature ramp of 10 °C/min

oxygen peak at 560 °C is 1½ times the area of the 950 °C peak, while the combined area of the small, broad peaks at 590 and 695 °C is ½ of the area of the 950 °C peak. Summing these up, it appears that half of an O_2 molecule $\{(1½ + ½)\cdot¼\}$ is emitted in the 500–700 °C temperatures range, most of it in a single well defined sharp step, while the rest is emitted in a disorganized fashion, possibly during the emission of SeO_2.

By reexamination the DTG decomposition curve, one can compare the sharp peak at 490 °C to the sharp oxygen peak at 550 °C in the TPD spectrum. However, loss of $½O_2$ corresponds to 5.4 w/o weight loss while the weight loss of the 490 °C peak in the TG was 12.1 w/o. It is not unreasonable to assume that the completing theoretical mass loss of 6.7 w/o, is from SeO_2 emission through the formation of some unstable intermediate of the form $(CuO)_x(SeO_2)_y$. Indeed we observed several steps, the broad peaks in the 500–620 °C, in which different fractions of the theoretical mass loss of SeO_2 (37.4%) are emitted, ranging from ca. 3.6 to ca. 9.5%.

Conclusions

The results of this work conclude the thermal dehydration and decomposition of copper selenate pentahydrate in an inert atmosphere. The dehydration is a three-staged process constituting emission of 3½, ½ and 1 water of crystallization molecules reaching completion at 280 °C. The thermal decomposition of the dehydrated compound, as determined by complementary TG and TPD experiments, proceeds to copper selenite through loss of oxygen at 490 °C, followed by a transition through several unstable intermediates to copper oxide in the temperature range of 500–620 °C. Finally, between 820 and 900 °C, the copper oxide is reduced to Cu_2O.

References

1. Paulik J, Paulik F, Arnold M. Dependence of the thermal decomposition of $CuSO_4\cdot5H_2O$ on the experimental conditions. J Therm Anal. 1988;34:1455–66.
2. Paulik F. Special trends in thermal analysis. Chichester: Wiley; 1995. p. 121.
3. Sedlak JM, Beebe RA. Pseudo-phase changes in cupric sulfate pentahydrate during dehydration. Thermochim Acta. 1974;9:261–8.
4. Gospodinov G. Investigation of the isotherms of solubility in the system $CuSeO_4$-H_2SeO_4-H_2O at 25 and 100°C, the polytherm of solubility in the system $CuSeO_4$-H_2O, and some properties of the compounds obtained. Z Anorg Allg Chem. 1984;513;213–21.
5. Nabar MA, Paralkar SV. Thermal decomposition of some divalent metal selenates. Thermochim Acta. 1975;11:187–96.
6. Koleva V, Stoilova D. DTA, DSC and X-ray studies on copper and manganese selenate hydrates. Thermochim Acta. 1999;342:89–95.
7. Nabar MA, Paralkar SV. Studies on selenates: 2 . Thermal decomposition of heavier rare-earth selenate hydrates. Thermochim Acta. 1976;17:239–46.
8. Danon A, Avraham I, Koresh JE. Temperature programmed desorption-mass spectrometer with supersonic molecular beam inlet system. Rev Sci Instrum. 1997;68:4359–63.
9. Saig A, Danon A, Finkelstein Y, Kimmel G, Koresh JE. A continuous polymorphic transition of coordinating water molecules in $CuSO_4\cdot5H_2O$. J Phys Chem Solids. 2003;64:701–6.