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THERMAL ANALYSIS AND SYNTHESIS OF PENTAZINC HEXAHYDROXIDE DICARBONATE

INVESTIGATIONS BY THERMOGRAVIMETRY, THERMO MOLECULAR BEAM ANALYSIS AND X-RAY MEASUREMENTS

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ABSTRACT

A combination of thermobalance and X-ray camera is described which allows simultaneous thermogravimetric (TG) and X-ray measurements under high vacuum. During these measurements the sample is positioned in the sample holder of the camera in the usual fashion and is X-rayed while the temperature is varied. The molecular beam of the gaseous decomposition products flows through a connecting tube which acts as a molecular beam former between camera and thermobalance. The molecular beam is directed towards the empty balance pan. The orifice through which the beam exits as well as the pan have special shapes that allow transfer of the angular momentum of the decomposition beam to the balance. The exerted force is a function of time and corresponds to the first derivative of the TG curve, i.e. to the DTG curve. The integrated curve is directly proportional to the change in mass of the probe. A quantitative evaluation is possible if the molecular composition of the beam is known. The calibration of the molecular beam and the evaluation of the measurements will be discussed. The results show that simultaneous detection of X-ray scattering and indirect TG curves allows a better interpretation of decomposition reactions.

An additional investigation shows that thermal synthesis of chemical compounds can also be studied by thermogravimetry. Based on the same compound as described in the analysis, the pyrosynthesis is demonstrated. The special instrumentation and the test conditions are discussed.

THERMAL ANALYSIS OF PENTAZINC HEXAHYDROXIDE DICARBONATE

Introduction

A considerable time ago X-ray analysis established itself as an important tool in the fields of crystal and analytical chemistry, as well as in solid state chemistry and physics. Today this method for obtaining information on purity, structure, lattice defects and crystallinity of chemical compounds is a routine method in the chemical laboratory[1–4]. With the introduction of variable temperature X-ray cameras and diffractometers this technique was extended to temperature-dependent experimental investigations. Many physical and chemical processes can in this way be continuously observed as a function of temperature. These include, for example, measurements of thermal expansion, the investigation of the temperature dependence of phase transitions in systems of one or more components, epitaxial growth, recrystallization rates, determinations of particle size, and others[5–7].

It is also a frequent practice in thermoanalytical work such as thermogravimetry and differential thermal analysis to investigate the course of reactions like decompositions or phase transitions in solid compounds through heating to a certain temperature and subsequent X-ray analysis on a discontinuous basis. However, quite often this procedure causes difficulties because the sample changes its composition during cooling and transfer to the X-ray equipment so that its state does not correspond any longer to the experimental conditions. For example, it is usually not possible to investigate metastable states in this fashion. It is therefore very natural to look for a method that allows the simultaneous application of the usual thermogravimetrical technique and X-ray analysis.

Principle of measurement and apparatus

For technical reasons it is comparatively difficult to carry out thermogravimetric measurements simultaneously with X-ray analysis, i.e. to continuously X-ray the sample while it is being heated on the pan of the balance. Therefore, a different way was chosen to obtain information on the change in sample weight; a way which allows one to leave the sample in the sample holder of the X-ray camera, to X-ray continuously in normal fashion while heating the sample, and still be able to record the change in weight of the sample during the reaction.

The measurement of the change in weight occurs through the gaseous decomposition products that are generated during the decomposition and which are brought from the camera to the thermoanalyzer via a vacuumproof link. These gases form a molecular beam that hits the pan of the balance. Orifice and pan, both have special flat shapes such that the arriving molecules bounce back and forth several times before they exit at the side and are removed by the vacuum system. The impact of the bouncing molecules exerts a force on the pan of the balance. The recorded curve of this force is proportional to the first derivative of the sample weight, or, in other words, under certain conditions the area under the peak of the curve is directly proportional to the total change in weight of the sample. We call this analytical method "Thermo Molecular Beam Analysis (TMBA)".

This method was implemented in our laboratories with the aid of a Mettler Thermoanalyzer[8], an Enraf–Nonius high-temperature camera[9] (System Lenné) and a Balzers Quadrupole Mass Spectrometer[10]. As can be seen from Fig. 1 the camera is mounted directly above the thermoanalyzer. The furnace of the camera is connected to the heated system of the impact plates of the balance via a vacuumproof link. This linking conductor has to be heated during an experiment. A valve permits one to seal off the vacuum of the balance during the changing of the sample. Therefore, only the camera has to be opened and re-evacuated for this operation.

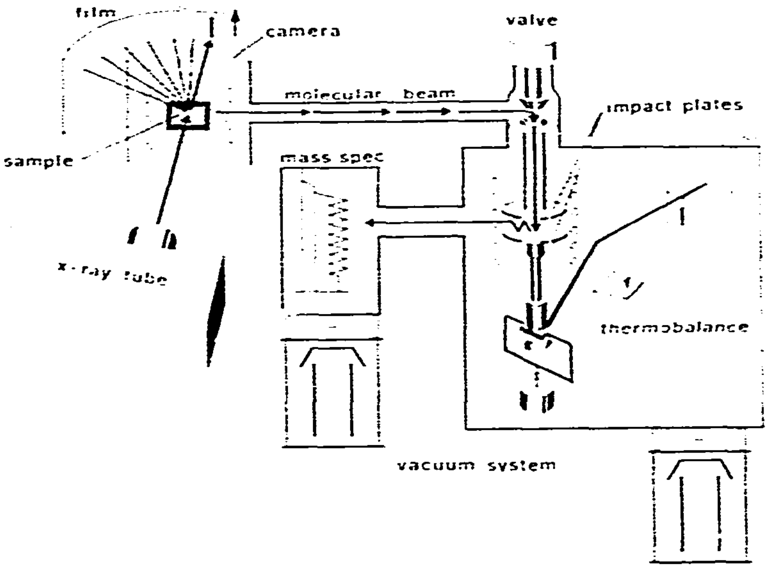


Fig. 1. Schematic diagram of the thermobalance, X-ray high-temperature camera and mass spectrometer.

The samples are spread on a platinum wire mesh and are mounted in a sample holder which is in direct contact with the thermocouple which indicates the temperature of the sample. The camera is attached to an adjustable frame to which the cover of the X-ray tube holder is directly connected. This focusing camera uses a quartz monochromator. The film holder that contains the X-ray film is part of a transport system that allows the film to be passed at various speeds in front of the X-ray exit slit and exposes it synchronously with the temperature sweep. The exit slits can be adjusted between 1 and 5 mm.

The temperature of the furnace in the X-ray camera is controlled with the temperature control equipment of the thermoanalyzer. Heating rates used are mostly between 0.1 and 4 °C min^{-1}. The present furnace allows a maximum temperature of 1200 °C. The temperature of the impact plates can be set anywhere between room temperature and 450 °C and remains constant (± 2 °C) during an experiment. It is recorded continuously together with the other measurements. The spacing between the impact plates is variable between 0.5 and 4 mm and can be set to within 0.01 mm with the aid of a micrometer.

The X-ray tube is connected to a commercial generator. If a switch is provided other cameras for other types of analysis can be operated alternatively. After an experiment the X-ray film is developed and measured on a photometer. Time markers on the film allow the comparision of the spectral information with the recorded curves. The quadrupole mass spectrometer helps in the evaluation of TMBA by providing quantitative information about the percentages of the molecules that make up the beam. For the rest, the experiment corresponds to a regular thermogravimetric analysis.

Determination of changes in weight in thermogravimetric investigations with molecular beams

In TMBA the reaction, as was mentioned earlier, is described by a curve that forms one or several peaks representing the change in sample weight as a function of temperature. This means that the impacting gaseous decomposition products transfer momentum to the pan of the balance which is recorded as a force. This force is directly proportional to the rate of weight change if all the molecules of the decomposition reaction arrive at the pan under isothermal and isobaric conditions and if there occur no reactions, associations, dissociations, condensations or absorptions on the way.

Two methods were used to calibrate the measured peak areas of decomposition reactions. The first method consists in decomposing thermally a known compound and consecutively relating the calculated weight decreases to the peak areas. In the second method a decomposition reaction is simulated with an injection system (Fig. 2) with which known amounts of a pure gas can be injected into an evacuated gas pipette under isothermal conditions. By means of a servo controlled valve the gas is then made to leak into the beam conductor and plate system. The peak areas of the curves have been determined digitally with the aid of a digital voltmeter, a Mettler data transfer unit, and a paper tape punch. The results of the measurements show a standard deviation of about 2%. Examples of calibration data[11,12] are shown in Fig. 3. Figure 3D shows that for various gases the ratio between the square root of the molecular weight or the mean velocity of the molecules and the determined area remains constant. Deviations essentially relate to the different atomicity of the gases. Hydrogen and helium are not within the scope of this diagram because of their high heat conductivity.

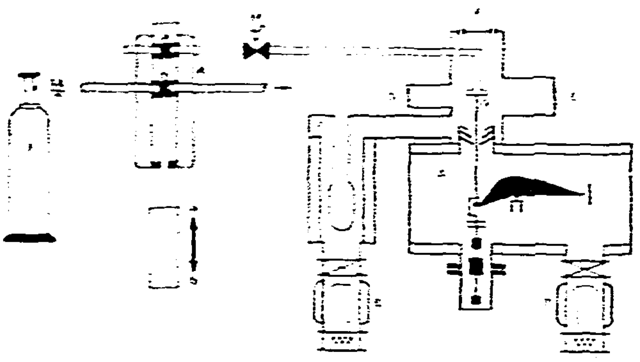


Fig. 2. Thermobalance with a gas injection system that is used to calibrate molecular beam forces.

Further results are summarized in a number of other diagrams. Diagram A shows the dependence of the measured peak area on the distance of the impact

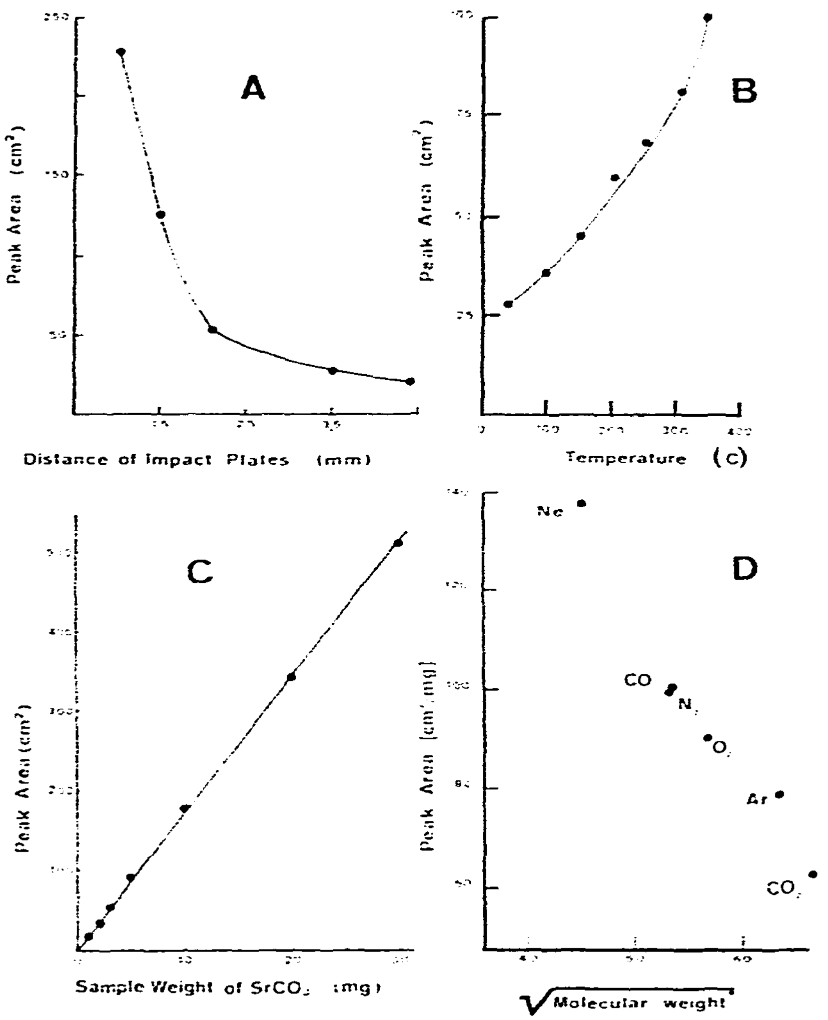


Fig. 3. Diagrams showing the molecular beam forces (expressed as peak area of recorded curves) as a function of various parameters.

plates. The dependence of the peak area as a function of the plate temperature is represented in diagram B. Another diagram (C) confirms the linearity between the measured peak area and the amount of gas that hits the plates. This, for example, has been shown for CO_2 produced in the decomposition of different amounts of strontium carbonate.

In summary one can say that within the range of certain experimental parameters the curves of the thermal molecular beam technique can be used for quantitative analysis. It is necessary to use a mass spectrometer for the evaluation of complex decomposition reactions in order to be able to determine the percentage of the different contributing gases as well as to be able to detect any possible association or dissociation products.

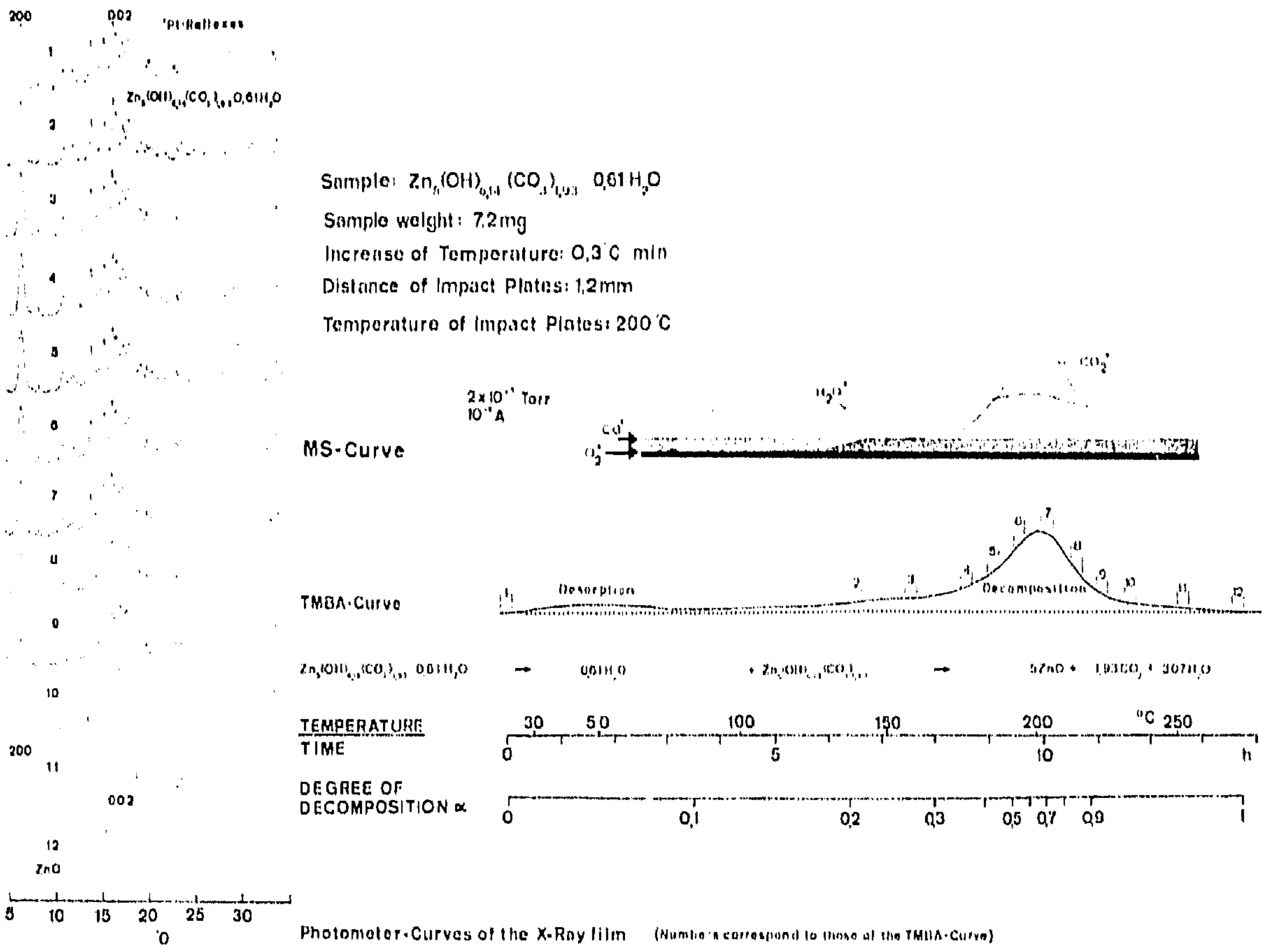


Fig. 4. Results of simultaneous TMBA–X-Ray–MS analyses in high vacuum.

Experimental results

Figure 4 represents the results of the thermal decomposition of synthetic basic zinc carbonate[13] that have been obtained with this method. For this investigation 7.2 mg of the compound were spread on a platinum wire mesh and heated in high vacuum with a rate of 0.3 °C min^{-1} from 28 to 335 °C and with 1.5 °C min^{-1} from 335 to 757 °C. We used Cu K_α radiation, 40 kV/25 mA, and a scan rate of 5 mm/h for the film. The TMBA curve shows first the evaporation of adsorbed water which is completed at 75 °C. Just a little later a small diffusion of H_2O and CO_2 occurs.

Starting from 170 °C the reaction is completely controlled by diffusion, i.e. the compound is now decomposing. Between 240 and 280 °C the change in weight slows down. This is due to the different diffusion rates of the ions caused by their size, and to absorption at the greatly increased surface of the new phase zinc oxide which can amount to up to 100 m^2 g^{-1}.

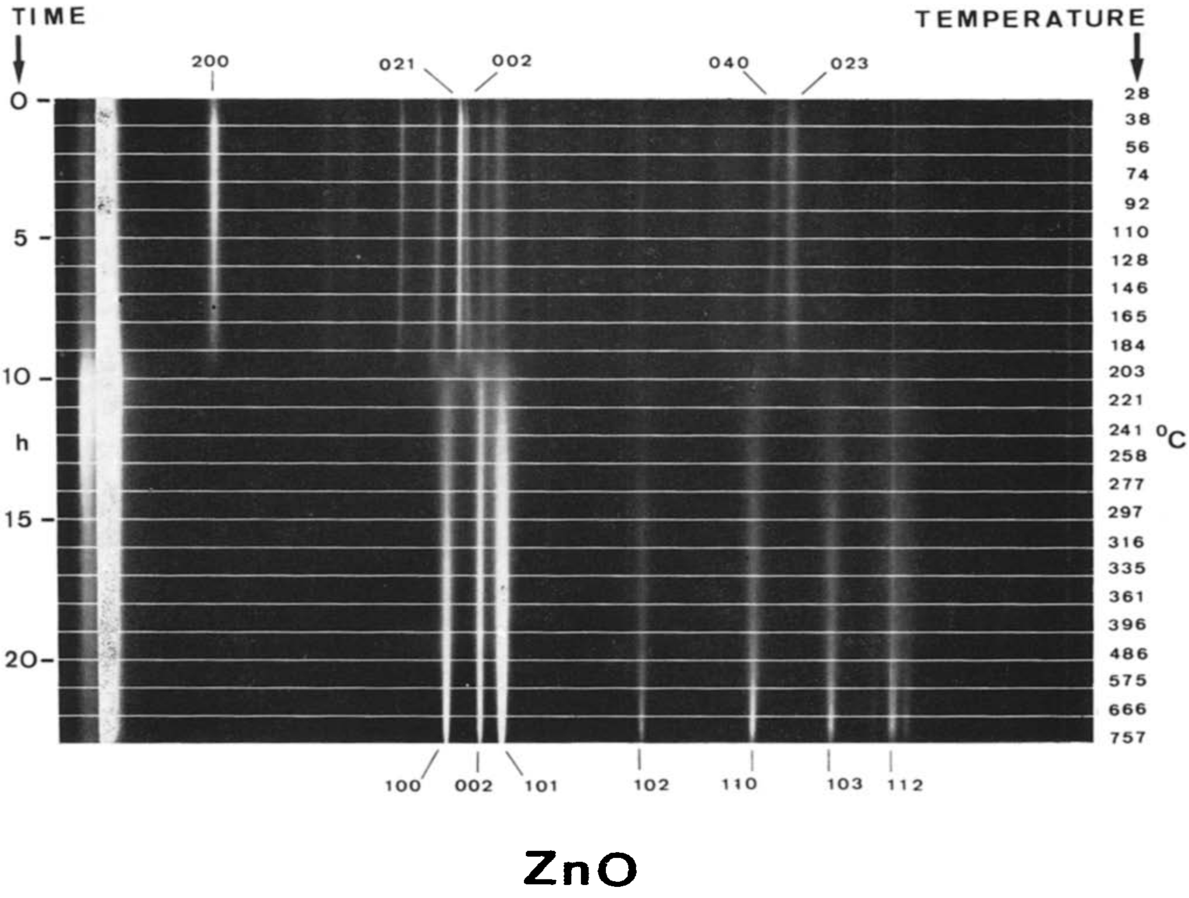


Fig. 5. X-ray film showing the thermal decomposition of $Zn_5(OH)_{6.14}(CO_3)_{1.93}$ 0.61 H_2O. Film speed: 5 mm/h, copper K_α radiation (40 kV, 25 mA). Heating rates: 0.3 °C/min^{-1} (28–335 °C) and 1.5 °C min^{-1} (335–757 °C). Other experimental conditions same as in Fig. 8.

The numbers of the photometer curves correspond to various temperatures given in the positions of the TMBA curves. The slit width used for evaluation in the photometer corresponds to 3.6 C or to a time of 12 min.

The photometer curves indicate that hydroxycarbonate (see the 200 reflex in Fig. 5) is present up to a degree of decomposition of $\alpha > 0.90$ in the decomposition whereas the 100 reflex of zinc oxide becomes visible at $\alpha = 0.70$.

The shift of the reflexes in the X-ray film (Fig. 5) as well as the photometer curves (Fig. 4) show a contraction in the *c* axis (see the 002 reflex) and an expansion in the *b* axis (see the 040 reflex) of the crystal. They provide information about the changes in the unit cell that occur during the decomposition reaction. A scanning electron micrograph of a single crystal of hydrozincite (Fig.6), which was heated in the same way as the synthetic material, confirms the changes by showing fissures and cracks in the direction of these two axes. Analytical investigations of the residues indicate that with increasing degree of decomposition in high vacuum the proportionality for the OH^- and CO_3^{2-} ions is not kept due to the different diffusion rates (Fig. 7). This is likely to be the reason for the changes observed and described above. By the test in dry air the same effects can be observed as in high vacuum, excepting that CO_2 escapes more quickly and due to subsequent reaction with the water OH^- ions are in a majority when the decomposition is terminated. In opposition to these measurements investigations in moist air show neither a disproportion of the residue nor a change in the diffraction pattern.

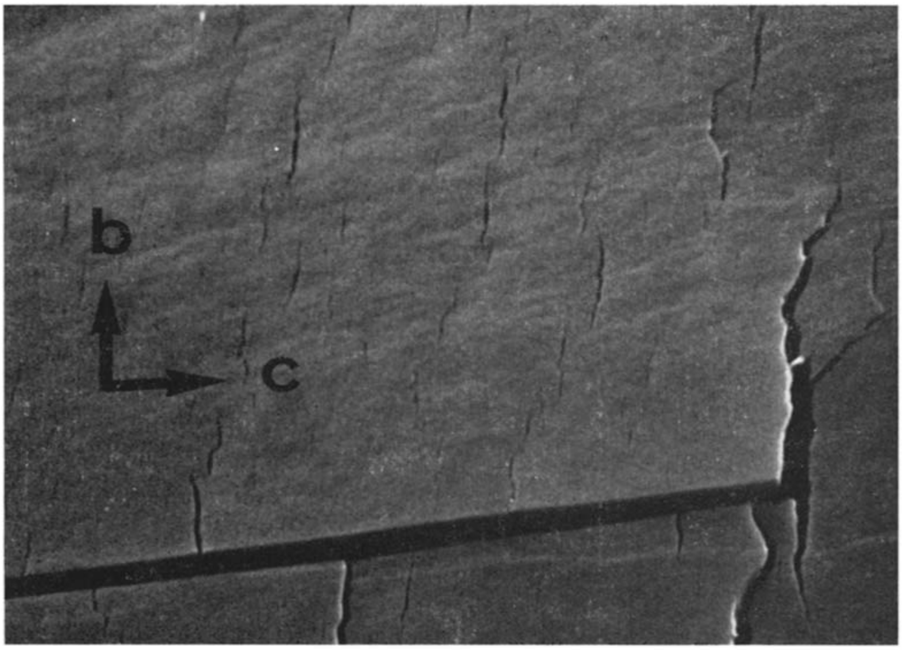


Fig. 6. After decomposition a hydrozincite single crystal shows fissures and cracks mainly in the direction of the *b* and *c* axes (magnification 5000 ×).

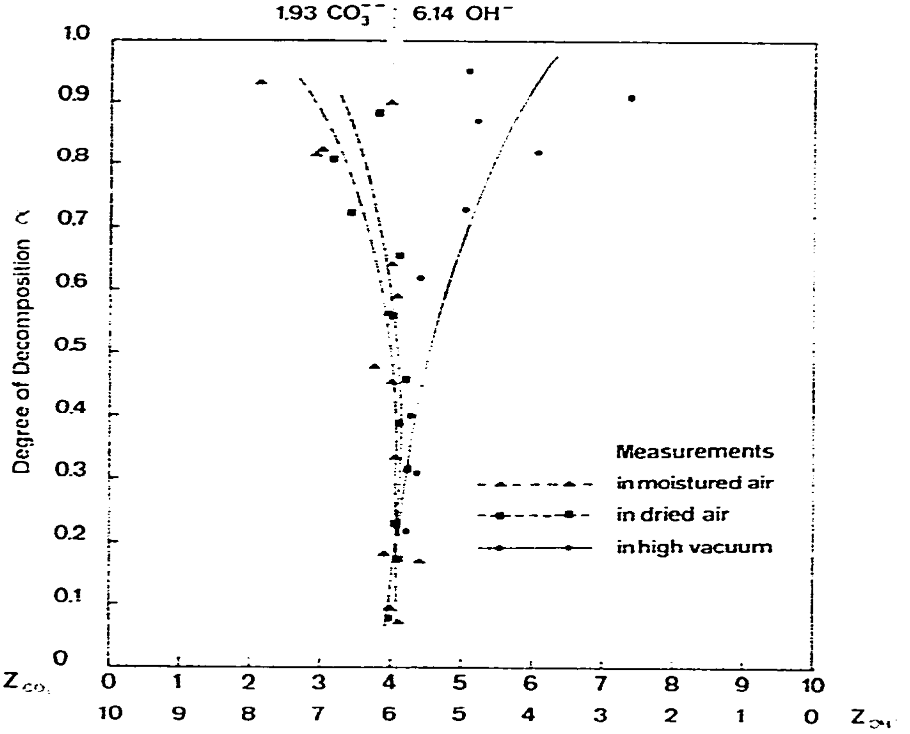


Fig. 7. Distribution of charge contribution of ions during the decomposition in various atmospheres.

If the samples are heated to even higher temperatures, it is possible to calculate[14-16] the variation of particle size and recrystallization rate from the decrease of line broadening in the diffraction pattern (Figs. 5 and 8). The results allow one to determine the change of specific surface of the decomposition product during the heating periods. Figure 9 shows the change of the specific surface area as a function of the highest temperature. These results may be compared with those obtained by other methods.

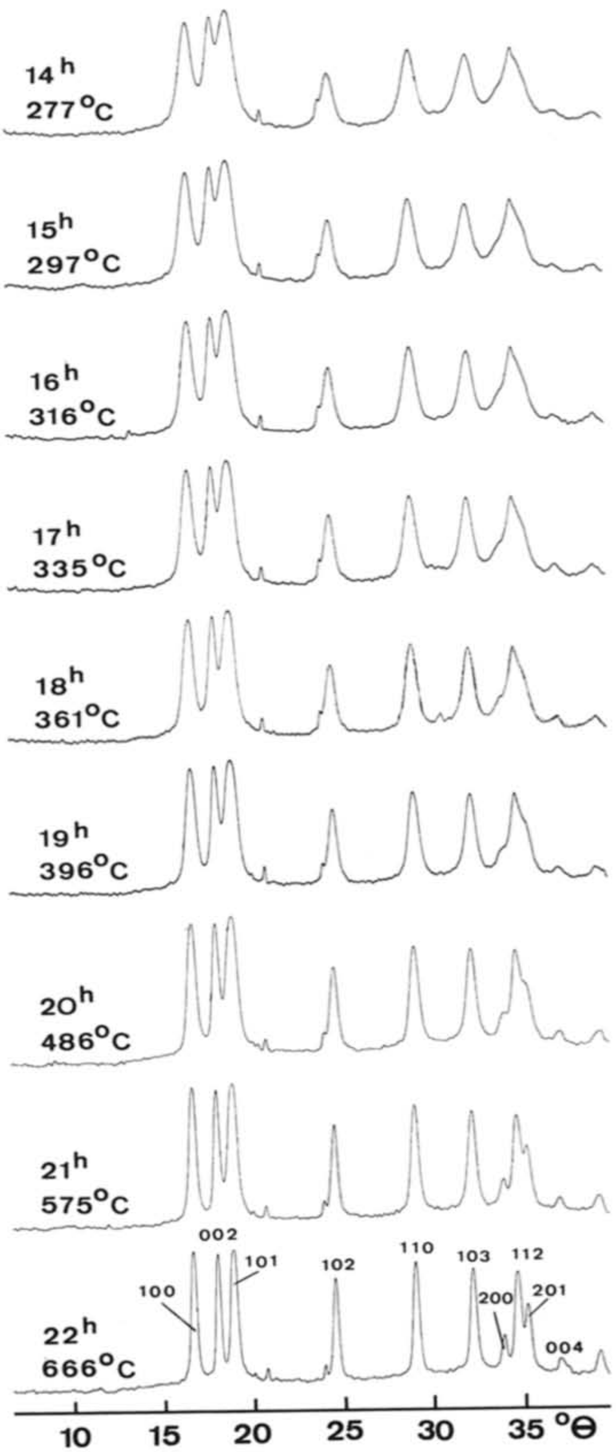
In this reaction a topotactic relation can be recognized. The 002 reflex of hydroxycarbonate and zinc oxide show only a small change in their placement. This means that the nucleation of the new phase may continue from there.

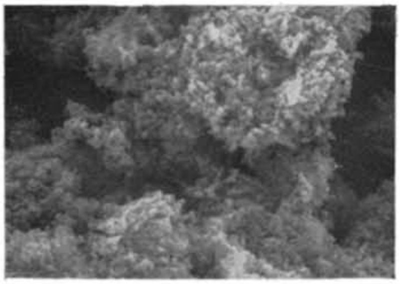
The relation between the change in intensity of the reflexes and the advancement of the reaction cannot be compared in decomposition reactions of many compounds because solid solutions are formed between the old and the new phase.

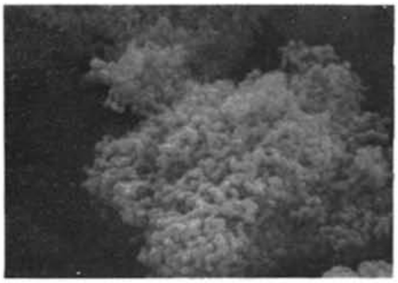
THERMAL SYNTHESIS OF PENTAZINC HEXAHYDROXIDE DICARBONATE

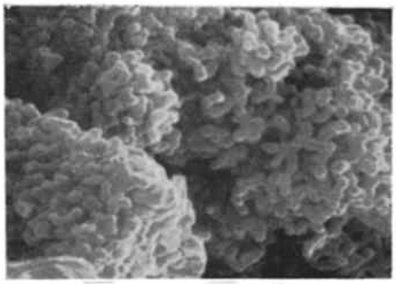
Introduction

Investigations made by Zaugg[17] several years ago on the reaction of solid hydroxides with gaseous carbon dioxide and water vapor have shown the formation of compounds similar to pentazinc hexahydroxide dicarbonate. The quantitative




ZnO at 600°C


ZnO at 700°C


ZnO at 800°C

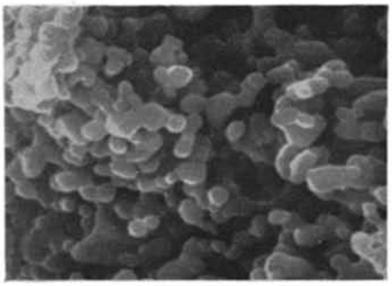

ZnO at 900°C

Fig. 8. Various photometer curves of the X-ray film shown in Fig. 6. The dependence of the reflexes on the temperature indicates increasing ordering and recrystallization of the ZnO which was formed. This behavior is confirmed by photographs (magnification 10 000 ×), taken with an electron microscope.

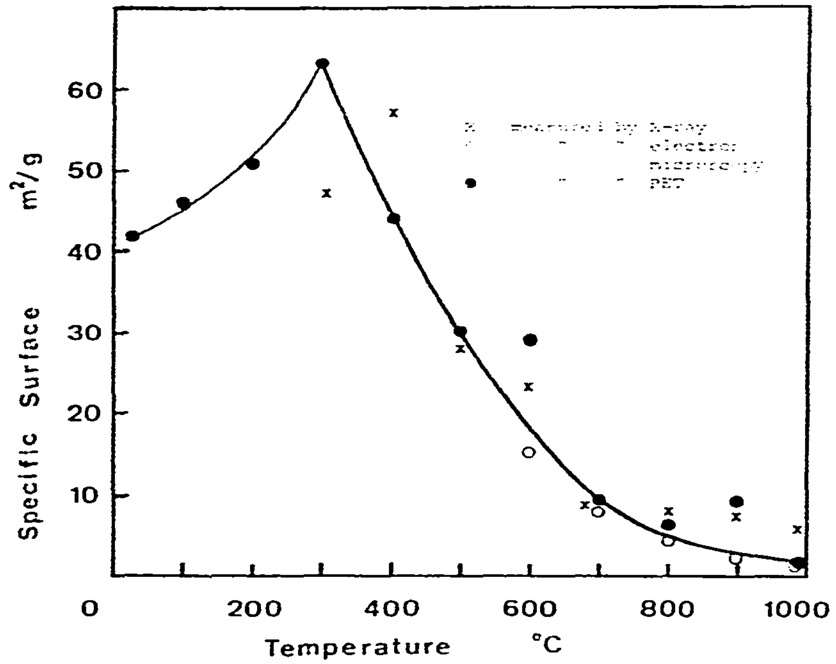


Fig. 9. The X-ray film (Fig. 6) allows the determination of the change of specific surface of the decomposition product (ZnO), which was formed during the decomposition of zinc hydroxicarbonate. Measurements taken with other methods where the sample were heated to the corresponding temperatures, are in good agreement with those obtained by the X-ray method.

analysis yielded a composition of

$$Zn(OH)_{1.3}\,(CO_3)_{0.35}\,(H_2O)_{0.12} \triangleq Zn_5(OH)_{6.5}\,(CO_3)_{1.75}\,0.6\,H_2O.$$

It was, therefore, pertinent to study, under similar conditions, the behavior of the active zinc oxide[14] that was formed during the thermal decomposition.

In a series of investigations tests were made to establish how far the zinc hydroxide carbonate (Merck), which was completely decomposed to zinc oxide in an atmosphere of CO_2–H_2O vapor, could be synthesized again during the linear programmed cooling. As described in the following, a special furnace (Fig. 10) was developed for this kind of investigation[18].

Principle of the apparatus used

A gas mixture of carbon dioxide and water vapor had to be used in the furnace of the thermobalance for the pyrosynthesis of basic zinc carbonate. Figure 10 illustrates schematically the system for these tests. The crucible "B" containing the substance is placed on top of a sample holder in the center of the furnace heating zone. The sample holder is attached to the balance stirrup. In the flask "A" water vapor is generated, which is carried by the gas entering at "C" into the furnace through the insulated connecting tubes. The condensed water runs back to the flask "A". The gas entering at "D" flows up through the balance and inner gas flow tube and prevents water vapor from the furnace entering the balance housing. The gas exits at "E" after passing through the back flow condenser.

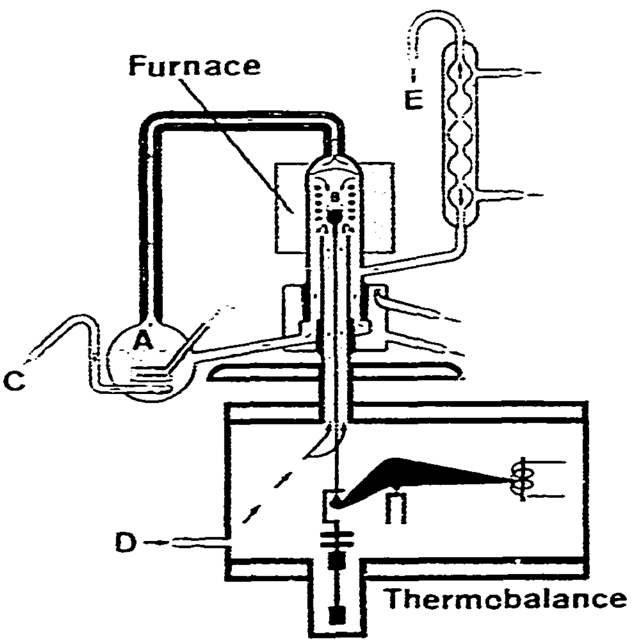


Fig. 10. Schematic sketch of the thermobalance with a furnace for special vapor atmospheres.

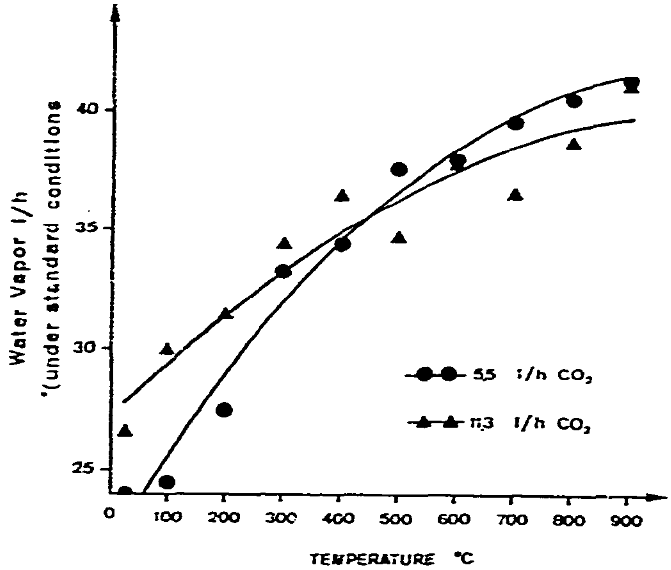


Fig. 11. Diagram showing the water vapor transport for two gas flow rates of CO_2 through the reaction chamber (furnace of the thermobalance) as a function of temperature under standard conditions* (20°C and 760 torr).

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* Pt-reflections from the platinum wire mesh.

Measuring the amount of water vapor passed through the furnace is possible only by feeding the water condensate into a graduated measuring cylinder instead of draining it back into flask "A". To compensate for the evaporated water, flask "A" has to be continuously replenished by a drop feeder. If, for isothermal conditions, a constant gas flow through the flask "A" is used, the amount of water vapor carried by the gas into the furnace is also constant. The amount of water vapor carried along by the gas will constantly change with the temperature, when a linear heating rate is used for dynamic studies. Tests were, therefore, made to establish the amount of water vapor that flows through the reaction chamber of the thermobalance at different temperatures. Results are shown in Fig. 11 for two different CO_2 gas flow rates. The curves show the water vapor flow measured as condensate, as a function of temperature.

Experimental

The zinc hydroxide carbonate sample (Merck) was weighed on the thermobalance and linearly heated or cooled in the water vapor furnace. The H_2O–CO_2 atmosphere was generated, as already indicated, by a flow of CO_2 through the water vaporizer (flask "A") into the sample chamber. The condensed water flows back into flask A, the CO_2 exits through the gas outlet. An additional flow of CO_2 through the balance prevents any water condensation in the balance chamber or on the sample holder. The tests could only be started after both CO_2 gas flows were adjusted to a constant rate and the vaporizer showed a constant return flow of condensed water. Flowmeters were used to adjust and control the gas flow rates.

Preliminary tests

Preliminary tests first clarified what reactions took place, if one of the two gas phases, water vapor *or* carbon dioxide, were used separately.

A sample of pentazinc hexahydroxide dicarbonate, which served as the basic test substance, was first decomposed in a gas stream of CO_2-free air and water vapor (5 l/h). The tests showed that the resulting zinc oxide picked up only negligible amounts of water during fast, or even stepwise isothermal cooling, even for long periods of time (5 h), independent of maximum test temperature (500 °C). This means no hydroxide carbonate was formed. Samples treated in this way showed a normal, unchanged zinc oxide pattern on the X-ray films, the same as obtained from normal decompositions. If instead of the air–water vapor mixture only carbon dioxide is used as gas atmosphere under otherwise unchanged conditions, only the decomposition temperature is moved to a higher value. The weight increase during cooling in the CO_2 atmosphere lasts only until the water vapor, generated during the decomposition, is flushed out by the CO_2 stream. Only then is the reverse reaction finished and the residue weight constant; i.e., without H_2O vapor no reformation of the hydroxide carbonate takes place. X-rays show only unchanged zinc oxide.

Only with water vapor *and* carbon dioxide as test atmospheres, after the thermal decomposition of zinc hydroxide carbonate, a definite weight gain of the zinc oxide remaining in the crucible was noted straight after cooling. Dependent on the test temperature, the weight gain started between 200–100°C. During the preliminary tests, a sample of zinc hydroxide carbonate was heated to near complete decomposition at 252°C and cooled after a half hour isothermal hold. X-rays of the residue showed the interference bands were similar to the ones of zinc hydroxide carbonate, but that compared to the original product (Merck) additional interference lines were present. These interferences are also present in X-rays of a natural product (Good Springs, Nevada), which leads to the conclusion that this resulting product is made up somewhat different from the original product (Merck). The differences in the location of the interferences (slight shifts could be detected), led to the conclusion of expansions and contractions in different directions of the grid structure. Interference lines of ZnO, however, did not appear, proving the complete change to hydroxide carbonate.

Measurements

A series of tests should establish the effect of different maximum test temperatures on the reformation of hydroxide carbonate from the zinc oxide phase. In addition, the flow rates of the gases or vapors, respectively, required for the reaction were varied. The resulting data are summarized in Table 1.

TABLE 1

TABLE OF DATA FROM TESTS TO SYNTHESIZE ZINC HYDROXIDE CARBONATE

No.	*WV No.*	*Sample weight (mg)*	*Heating/ cooling rates (°C/min⁻¹)*	*Length of isothermal hold @ max. temp.*		*Gas mixtures*	*Flow rates (hr^{-1})[b]*	*X-Ray film No.*
				min.	*(°C)*			
1	179	100.4	10	20	400	CO_2–H_2O	9/4	W47/1/69
2	177	100.02	10	20	500	CO_2–H_2O	9/4	W47/2/69
3	185	100	10	19	600	CO_2–H_2O	9/4	W47/4/69
4	175	200	10	20	600	CO_2–H_2O	9/3	W49/1/69
5	183	100	10	20	225	CO_2–H_2O	9/9	W47/3/69
6	181	100.03	10	20	300	CO_2–H_2O	9/9	W49/2/69
7	180	200.03	10	25	225	CO_2–H_2O	9/16	W49/3/69
8	182	200	10	130	300	CO_2–H_2O	9/16	W49/4/69
9	184	200	10	30	400	CO_2–H_2O	9/23	W48/1/69
10	176	200	10	20	500	CO_2–H_2O	9/23	W48/2/69
11	174	200.01	10	33	590	CO_2–H_2O	9/23	W48/3/69
12	178	200.06	10	20	600	CO_2–H_2O	9/23	W48/4/69

[a] A gas mixture of carrier gas and water vapor was used inside the reaction chamber for these tests. An additional flow of dry carrier gas was directed through the balance and into the reaction chamber (see Fig. 10). [b] The two values in this column refer to the two carrier gases used (through vaporizer/through balance). No flow rate for water vapor can be given; only a few approximate values are available from special tests. [c] Stepwise isothermal cooling of sample (e.g., in steps of 10°C). [d] Sample was repeatedly heated and cooled. [e] Sample was heated stepwise.

Figure 12 shows several resulting test curves of these measurements. The clearly visible weight gain at the beginning of the test trace is the result of water vapor adsorption on the original sample at room temperature. After constant flow conditions of the vapor mixture were reached, heating was started at 10°C min^{-1}. Due to heating an even larger amount of water adsorption is noted, until it is lost again after passing the 30°C mark. In the range of 50–100°C the adsorbed water is released again and the actual decomposition of the sample starts only then. Compared to air as atmosphere, the decomposition temperature is increased in a CO_2–H_2O atmosphere.

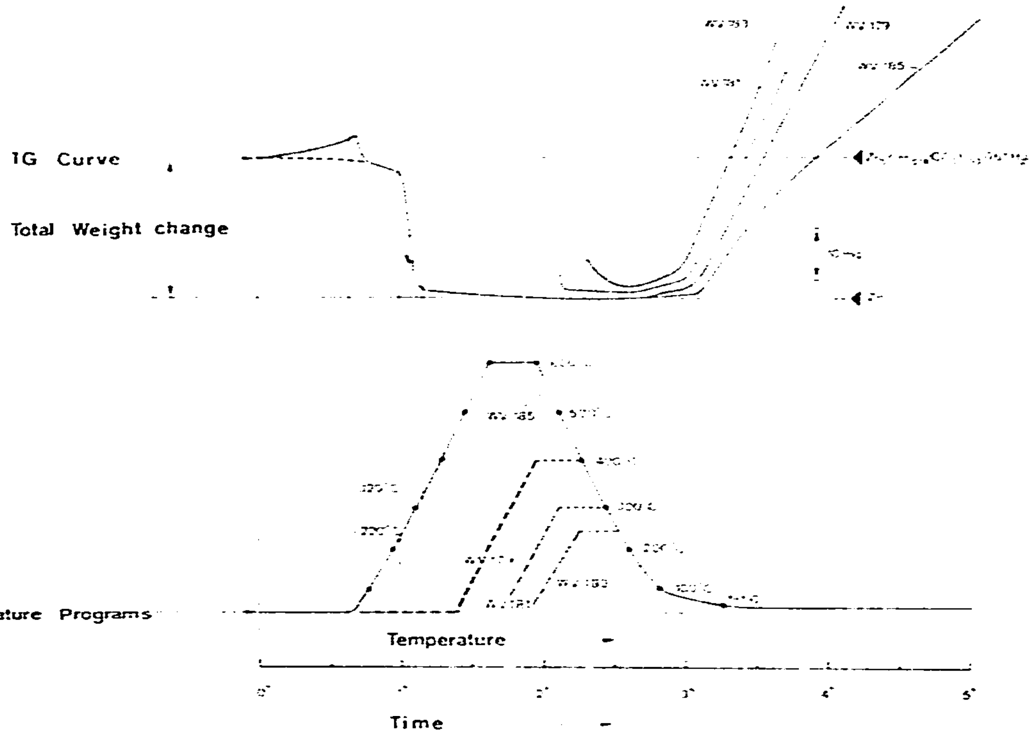

Fig. 12. Thermogravimetric curves from the decomposition and composition processes of pentazinc hexahydroxide dicarbonate as a function of different heating programs.

The decomposition is nearly completed from 300°C on. Continuous heating to 600°C yields only little additional weight loss, until pure zinc oxide finally remains. During each test, the sample was held isothermal for a certain amount of time after reaching the corresponding maximum test temperature, to enable it to establish decomposition equilibrium. During the following cooling, a noticeable weight gain was detected between 200–150°C.

The weight traces in Fig. 12 illustrate that the weight gain happened at different rates for the same cooling conditions. The reason for this behavior can primarily be found in the different maximum test temperatures of the preceding sample decomposition. For example, the substance heated to 245°C was not completely decomposed and picked up water and CO_2 fastest, whereas samples heated to more

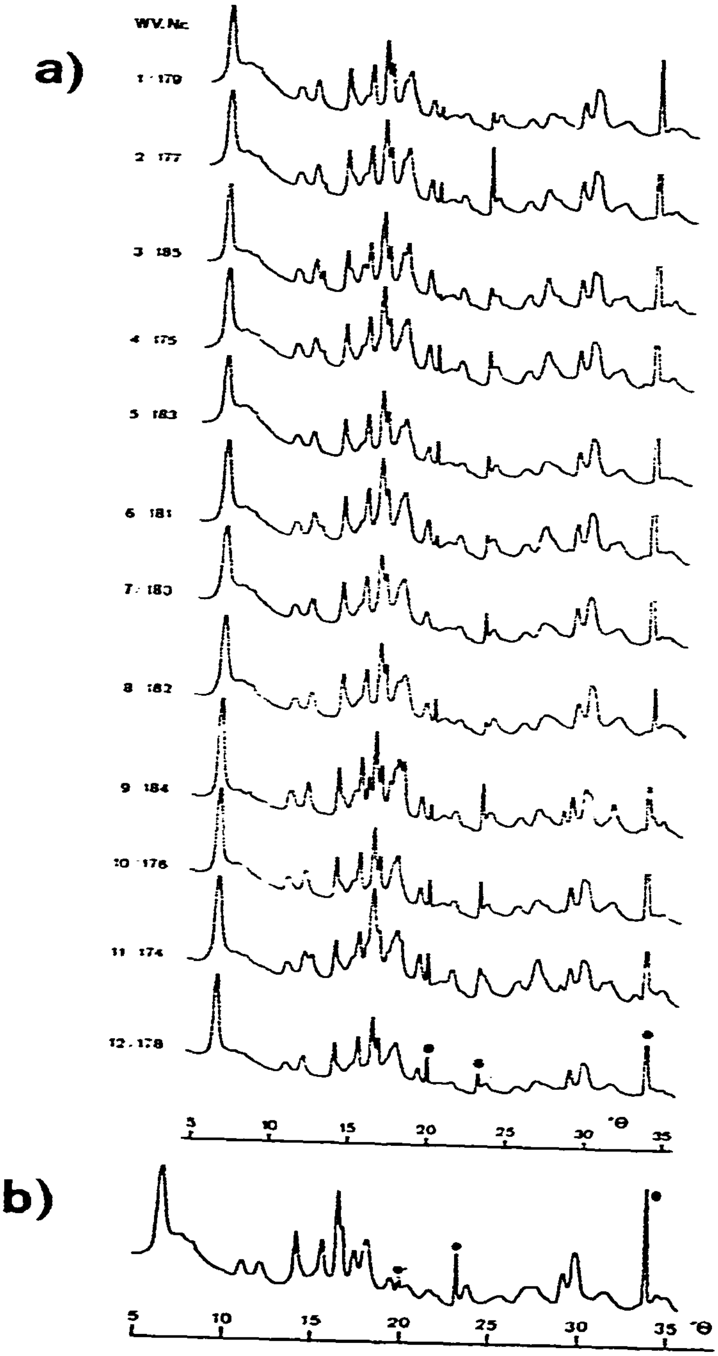

Fig. 13. (a) Photometer curves of X-ray photographs of the pyrosynthetic products from zinc hydroxide carbonate. (b) Photometer curve of the X-ray photograph of zinc hydroxide carbonate (Merck No. 8808). • Pt-reflections from the platinum wire mesh.

than 700°C showed no significant weight gains (approx. 2–3%) even after several days. The reason for this behavior can, among others, be associated with the change of the particle size of the resulting reaction product (see Fig. 6). Based on the particle growth that takes place at elevated temperatures, the specific surface area of the formed zinc oxide is reduced and hence the reaction with the gas environment is markedly slowed down.

Figure 12 illustrates the entire test trace for test WV No. 185. The sample decomposed while being heated to 600°C, with cooling following after a period of isothermal hold. Since the decomposition trace for all tests was identical, it is shown only once for reasons of clarity. For all other tests, only that portion of the test trace is shown that represents the weight gain during cooling. The dotted lines represent the temperature program for the corresponding test of which the weight gain traces only are shown. The weight gain of all traces shown exceeded the original stoichiometric weight loss of zinc hydroxide carbonate. A larger amount of CO_2–H_2O than originally lost was taken up by the sample.

Subsequent investigations showed that the reason for the larger weight gain was primarily adsorbed water. Comparisons of X-rays for both the samples with excessive weight gain and for those where the test was terminated when the theoretical weight gain was reached, did not show noticeable differences. Products synthesized in this way had to be dried in the desiccator before the analysis could be made.

Photometer curves from the X-ray photographs of all synthesized compounds are summarized in Fig. 13. Interference lines of ZnO are not present on any of the photometric curves of the decomposition product X-rays. The amount of decomposition products generated on the thermobalance was not sufficient to make several analyses to obtain average values. Therefore, only one value could be determined of each of the different preparations. This value compared to the data of Zaugg[14] about the composition of carbonated ε-zinc hydroxide yielded a certain agreement.

	Formula
Preparation from carbonated ε-zinc hydroxide[17]	$Zn_5(OH)_{6.5}(CO_3)_{1.75}\ 0.6\ H_2O$
Generated preparation of the second test series	$Zn_5(OH)_{6.6}(CO_3)_{1.70}\ 0.5\ H_2O$

DISCUSSION

The results of these qualitative investigations confirmed that a substance similar to pentazinc hexahydroxide dicarbonate is formed in a gas environment of CO_2–water vapor and a temperature range from room temperature to 200°C. The reaction takes place topochemically; i.e., the reaction mechanism can be imagined as follows: The relatively large surface area of the zinc oxide remaining after the decomposition adsorbs water first. The zinc ions as well as the necessary grid building blocks, such as CO_2, can now infiltrate this adsorption layer until, after nucleus formation of the basic zinc carbonates, they are incorporated into the new grid.

The path the reaction takes and its speed are, however, dependent on several factors. One of them is, for example, the level of the preceding decomposition temperature for the zinc oxide, particularly, if as in this case, it was formed from the decomposition of zinc hydroxide dicarbonate in moist air. The adsorption of CO_2–water vapor takes place relatively quickly if the oxide is not heated much above 600 °C after the decomposition. That means the speed with which the hydroxide carbonate phase is regenerated is dependent largely on the degree to which crystalites formed during the decomposition of the disoriented regions and grew epitactically out of zinc oxide nuclei to larger particles with smaller specific surface area.

The formation of hydroxide carbonate, which takes place during cooling of zinc oxide in a CO_2–water vapor atmosphere, started, as already mentioned, from the adsorption layer of water on the zinc oxide. The zinc ions which enter this layer react with the OH^- ions and the CO_3^- ions and again form hydroxide carbonate[19].

As the test showed, the formation of hydroxide carbonate and the speed at which this takes place are dependent on the composition of the test atmosphere, especially on the water pressure. The zinc oxide did not show any weight gain in a CO_2 atmosphere with a moisture ratio (p/po) less than 0.1 : i.e., no formation of hydroxide carbonate takes place. Only above a moisture ratio of 0.35 did the zinc oxide take up more water in a relatively short period of time than was necessary for the formation of basic zinc carbonate. In the moisture ratio range of 0.1–0.3, the formation was slower and did not lead to complete formation of hydroxide carbonate.

All samples for the tests discussed here were formed during more or less linear cooling. If, however, a stepwise isothermal cooling process was used and stopped above room temperature, a better crystalline substance was obtained. The X-rays of most substances formed in this way showed a change in the grid in the form of contraction and expansion. Attempts to make "fine range deflection" measurements failed due to the small size of the formed substance particles. The evaluation of the X-rays showed that the small crystals were expanded in the *a* and *b* axes and slightly contracted in the *c* axis.

CONCLUSION

The results shown indicate that the simultaneous measurement of change in weight and continuous X-ray provides a new insight which is not possible with separate determination. Besides analysis investigations, pyrosynthesis can also be studied by thermogravimetry. The measurements give information about the mechanism of the rebuilding process and aid understanding of some of the transport phenomena.

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