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Determination of activation energy in moist and dry conditions for the pyrolysis of $Zn_5(OH)_6(CO_3)_2$

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Abstract

Systematic work shows that the reaction rate and decomposition rate of $Zn_5(OH)_6(CO_3)_2$ depend on various parameters. The influence of the experimental atmosphere and the partial pressure of water are very important. The decomposition rates in moist air, dry air and high vacuum were determined.

INTRODUCTION

Measurements with different varieties of the natural mineral, i.e. hydrozincite (Good Springs, USA) and two synthetic hydroxide carbonates were carried out to investigate influences other than the atmosphere. Different sample masses were also used. All measurements were performed in platinum crucibles.

The dynamic measurement method was used for this analysis [1–3], i.e. the decomposition rate was determined during a linear temperature rise. The advantages and disadvantages of this method are discussed with the results at the end of this section.

The determination of the activation energy [4] is explained in a schematic diagram (Fig. 1). In this diagram the thermogravimetric decomposition curves are shown beside the simultaneously recorded temperature and DTG curves. The correlation of the TG and DTG curves with the corresponding temperature of the sample at the characteristic decomposition rate ($\alpha/2$) is shown by connecting lines. The weight loss rate $\dot{w}$ (mg min^{-1}), which is shown as a function of the decomposition time and

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Dedicated to Professor Joseph H. Flynn in honour of his 70th birthday.

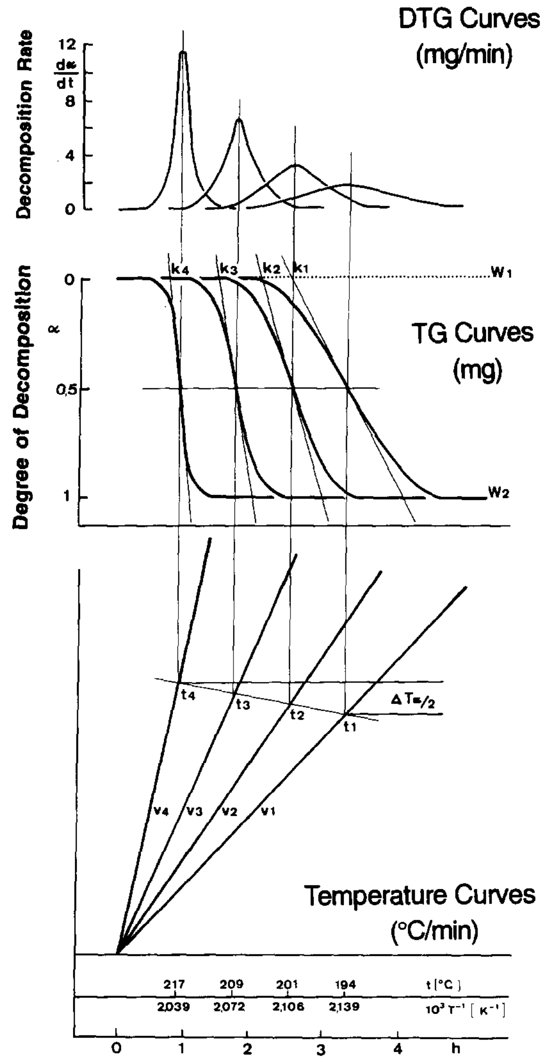


Fig. 1. Schematic diagrams of the determination of activation energies.

heating rate v, can be read directly. Normally, the characteristic decomposition rate is only slightly different from the maximum.

The temperature coefficient of the rate constant of each series was determined from the calculated differential quotient

$$d\alpha/dt = \dot{w}/(w_1 - w_2)$$

for each measurement made at a different heating rate (Table 1). The rate constant can be defined by

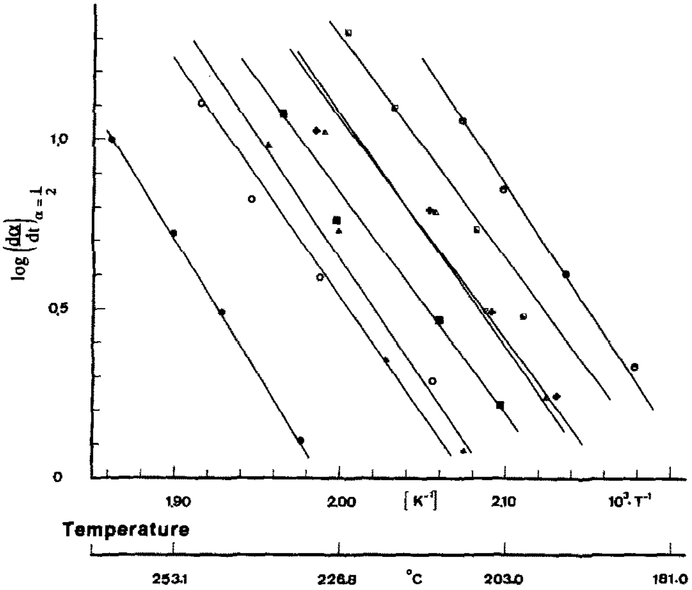
$$(d\alpha/dt)_{\alpha=0.5} = k = C\ e^{-E\alpha/RT}$$

TABLE 1

Temperature coefficient of the rate constant for different heating rates

Heating rate (°C min^{-1})	Decomposition rate (mg min^{-1})	Reciprocal temperature difference	Temperature coefficient of the rate constant $R/E_a(\partial \ln k/\partial T^{-1})_p$
v_1	dw_1/dt	$(1/T_1 - 1/T_2)^{-1}$	$(\ln \dot{w}_2 - \ln \dot{w}_1)$
v_2	dw_2/dt	$(1/T_2 - 1/T_3)^{-1}$	$(\ln \dot{w}_3 - \ln \dot{w}_2)$
v_3	dw_3/dt	$(1/T_3 - 1/T_4)^{-1}$	$(\ln \dot{w}_4 - \ln \dot{w}_3)$

The first term of the equation, the frequency factor C depends on the parameter α, a maximum limit per time unit of the successful events that lead at higher temperatures to rapid decay of the compound. The second



Hydrozincite	Sample (mg)	Ea (KJ/mol)
○ Good Springs, moist air	3.3	-130.7 ± 28.1
● Good Springs, dry air	3.3	-149.6 ± 2.9
Basic zinc carbonate		
● Merck product, moist air	3.3	-139.5 ± 6.7
■ Merck product, dry air	3.3	-124.9 ± 15.1
▨ Merck product, dry air	250	-125.3 ± 15.9
▲ ε - zinc hydroxide, dry air	3.3	-137.0 ± 13.0
▲ ε - zinc hydroxide, moist air	3.3	-132.4 ± 39.4
+ ε - zinc hydroxide, moist air	3.3	-126.5 ± 21.8

Fig. 2. Arrhenius plots, parameters and results of the measurements.

term has an energy contribution which normally has no theoretical significance in heterogeneous reactions, in contrast to homogeneous reactions, but according to experience it shows, within experimental error, a similar dependence on temperature and because of that it is defined as the activation energy E_a. The decomposition rates determined at $\alpha/2$ and the corresponding temperatures at different heating rates (0.5, 1, 1.5 and 2°C min^{-1}) can be represented in a coordinate system, as a function of $1/T$ in the form of a straight-line Arrhenius plot. The Arrhenius line is straight within experimental error, having a slope of $\log(\mathrm{d}\alpha/\mathrm{d}t)_{\alpha=0.5}$.

Figure 2 shows some of these results; the most important parameters are reproduced at the end of the diagram. The straight line in the middle was calculated by a linear regression ($y = a + bx$) from the results of the single measurements. The activation energy and standard deviation were calculated from the most probable gradient and experimental scatter.

All the obtained activation energies show that there are no significant differences at normal pressure, i.e. that the differences were insignificant in relation to the composition of the atmosphere, the sample size, the particle size, and the crystallinity of the experimental materials. The measurements in high vacuum, which were carried out later and are not shown in Fig. 2, vary considerably from the other results. The activation energy of the decomposition in high vacuum amounts to -185.2 ± 12.2 kJ mol^{-1}. The reason for the significantly higher activation energy is the very low partial pressure of water (1.33×10^{-3} Pa). Under other conditions this is considerably higher and promotes the decay.

There is apparently no significant difference between measurements in moist and dry air, because the free water that is formed during the decomposition has the same catalytic influence as the stationary water vapor atmosphere in the decomposition under moist air (at least up to a degree of decomposition $\alpha = 0.6$).

The dynamic method used (linear temperature rise) to determine the activation energy has an advantage over the statistical method (isothermal heating) in that it delivers results more quickly. But it should only be used for provisional measurements because of the more inhomogeneous temperature distribution in the sample.

The determination of the activation energy here shows only the kinetic temperature dependence of the rate of decomposition with otherwise identical experimental parameters. The frequency factor C can be quite different with a fixed parameter $\alpha = 0.5$, as the almost parallel but spread curves in Fig. 2 show.

DISCUSSION

The starting-point of this work [4] was to study the characteristics of the temperature dependence on the thermal decay of pentazinc hexahydroxide dicarbonate and some related compounds under different experimental conditions especially with respect to the gaseous atmosphere during the decomposition. Some previous experiments showed that one of the most important factors responsible for the rate of decomposition is the water vapour pressure.

The results of the measurements, performed at different water vapour pressures, lead to following hypothesis:

(1) If hydroxide carbonate is heated in an atmosphere of flowing moist air, layers of chemisorbed water are formed by the defect state of the crystal surface. The forces between the positions of this double layer structure, i.e. the ratio of the chemical bonding, is changed and the layer lattice distance is increased. There must be a connection between the structural changes and the promoted decay at low temperatures compared to the other experimental conditions (dry air and high vacuum): the thermal degradation is catalysed by the water of the water vapour.

The activation energies measured at different water vapour pressures during the decomposition also confirm the catalytic influence of the water. The results of the activation energy are -125.7 kJ mol^{-1} in moist air and -184.3 kJ mol^{-1} for the decomposition in high vacuum, both at $\alpha = 0.5$. Furthermore, there is a back reaction between the chemisorbed water layers and the ZnO formed which is mainly promoted by the water vapour pressure of the experimental atmosphere. The ratio of the hydroxide and carbonate ions in the residue changes with increasing degree of decomposition α by the development of CO_2 in the gaseous products of decomposition. The hydroxide ions are partly, or at least temporarily, converted into oxide and chemisorbed water.

(2) If the basic carbonate is heated in dry air, the decomposition proceeds with delayed water release, as it does in moist air. Later the reaction products dissipate, as occurs with water vapour during the decay in moist air. Lattice sites which were occupied by CO_3^{2-} groups are probably replaced by O^{2-} ligands and temporarily by OH^-. The X-ray diffractograms show an increasing lattice contraction during this process. A product is formed with an increased specific surface area. H_2O and CO_2 release then slows down and the decomposition is diffusion-controlled.

If the curves of the two decomposition diagrams are compared, it will be noticed that pyrolysis in dry air corresponds, up to a degree of decomposition $\alpha = 0.5$, to that in moist air. After that, however, it is similar to the decay in high vacuum.

(3) If the hydroxide carbonate is heated in high vacuum, the catalytic influence during the induction period is already reduced by the drying [5] and by the constant removal of reaction water. The decay is probably diffusion-controlled during the whole process.

The disproportion of the OH^- and CO_3^{2-} groups in the residue (Fig. 3), which was calculated as a ratio in the analysis, arises from the different

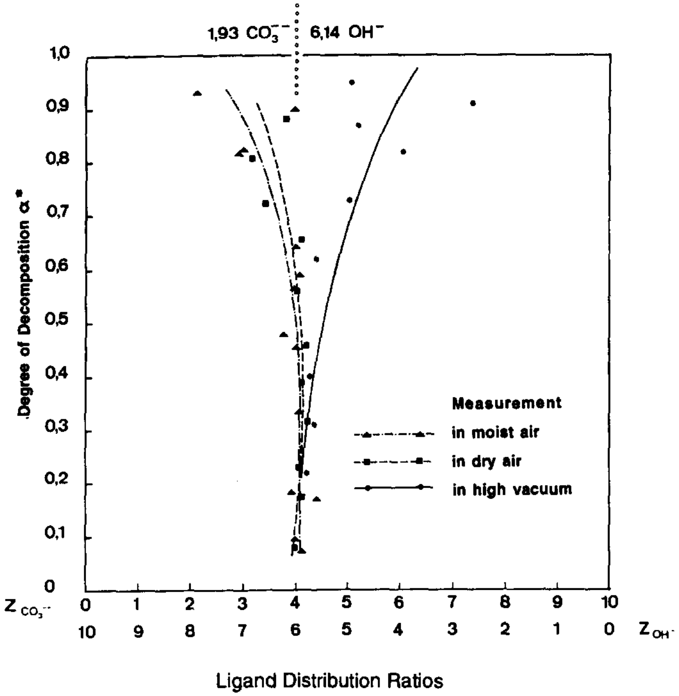


Fig. 3. Distribution of charge contribution of ions during the decomposition in various atmospheres. The degree of decomposition α * is here related not to mass change but to the original carbonate content.

evaporation rates of CO_2 and H_2O during the decay. There were not any observable structural changes in the X-ray diffractograms except for line broadening (line broadening indicates finely divided products and increased lattice disorder).

All three measurements (dry air, moist air, high vacuum) were each carried out in platinum crucibles with relatively high sample weights (approx. 250 mg) to allow for stepwise experiments, such that each residue could be analysed independently from the thermo-balance for ZnO, CO_2 and H_2O. Each residue was also analysed by X-ray diffractometry (Guinier de Wolff camera, Cu Kα radiation) and investigated in the electron microscope. In moist air the H_2O partial pressure was 2.36×10^3 Pa. In the high vacuum experiments, the vacuum was 5.40×10^{-2} Pa. The overall reaction can be written

$$1 \text{ mol } Zn_5(OH)_{6.14}(CO_3)_{1.93} \cdot 0.61H_2O \rightarrow$$
$$(5-n)/5 \text{ mol } Zn_5(OH)_x(CO_3)_y + nZnO + 0.39nCO_2$$
$$+ 0.62nH_2O + 0.61H_2O$$

The decomposition curves [4] indicate the following features of the reaction.

In moist air there is, in addition to the released water from the starting material, a water film derived from the air moisture which forms on the crystal surface and the ZnO nuclei. In this film, Zn^{2+} ions are mobile and larger crystallites of ZnO can grow. They can also reorganize their lattice better than in the absence of water.

CO_2 is continuously removed by the flowing air (or by the vacuum) and it therefore plays an unimportant role compared to the adsorbed water.

The chemisorbed H_2O molecules release a proton to the ZnO nuclei and the ZnO crystallites are covered with an outer layer of OH^- ions from the beginning.

The analytical results in moist air indicate this continuous increase of OH^- ions during the reaction. On this outermost OH^- layer, a film of molecular water builds up.

X-ray reflection profiles show that the ZnO becomes more crystalline under these circumstances: crystallites grow and they are more ordered.

The incipient decomposition in dry air and in a vacuum is the same. Very soon, however, CO_2 and, in particular, H_2O removal from the residue become very efficient. The reaction becomes a diffusion-controlled mechanism. The smaller ZnO crystallites (and hence the higher specific surface) inhibit diffusion.

Up to a rate $\alpha = 0.5$ the curve for dry air is virtually identical with that for moist air. Beyond $\alpha = 0.5$, however, the dry air reaction curve begins to resemble more and more the reaction curve for high vacuum. In a vacuum, the catalytic influence of water is reduced at an early stage and then disappears. Broadened X-ray reflection profiles in the product ZnO indicate smaller and less ordered crystallites. The water content in the product in dry air and vacuum conditions is not sufficient to form a coherent film of adsorbed molecular water in which the Zn^{2+} ions can move. This prohibits crystallite growth and lattice reorganization at the relatively moderate temperatures considered (approx. 170–210°C).

This has also been confirmed by the electron micrographs of the residue, which show that the platelets develop cracks during the decomposition. Crystals decay by the development and growth of decomposition nuclei (ZnO). Under low water vapour pressure, little adsorbed water is released and the growth of the ZnO crystallites is low at these temperatures.

In all three series discussed, ZnO reflections appeared in the X-ray patterns at a mass change of 50%. ZnO produced in stabilized quantities of the same kind of intermediate product could already be measured at a molar change of about 2%. This effect may probably be explained by the development of a solid solution of zinc oxide in hydroxide carbonate. Table 2 shows the concentration of zinc oxide in the different experimental series, as analytically detected after the experiment by the first appearance of X-ray reflections in the diffractograms. Figure 4 shows the decomposition rate plotted as a function of time for the three experimental conditions.

TABLE 2

Experimental time and temperature at which ZnO is first detected in the XRD patterns, and the concentration of ZnO found

Test	Experimental time	Temperature (°C)	Mole ZnO/atoms Zn_{total} (%)
Moist air	8 h 30 min	173.0	2.39
Dry air	6 h 30 min	196.1	1.94
High vacuum	3 h 25 min	202.0	1.99

Measurements of single crystals with a polarization microscope also showed that the pyrolysis nucleates at defect sites on the crystal edge and on the surface. From there the reaction zone extends spherically from the decomposition centre.

Cracks can be noticed after a certain decomposition time. Disordered domains, which grow with proceeding reaction, develop in the original crystal because of the release of the decomposition products CO_2 and H_2O. Adsorbed water develops from reaction water and oxide forms in this water film. Thus, the zinc oxide domains become organized, and with time and volume, shrinking cracks are produced. It is possible that because of the cracks, the diffusion channels of the reaction gases become wider and the pathway shorter. The developing CO_2 and H_2O diffuse through the cracks in the crystal and through the pore system of the oxide. The initial microcrystalline zinc oxide is pseudomorphous and becomes more organized later on heating.

Because some important lattice directions of the initial substance and the end product remain the same, the reaction may be called topotactic.

Qualitative investigations have shown, that a non-stoichiometric variety similar to the pentazinc hexahydroxide dicarbonate, is formed from the

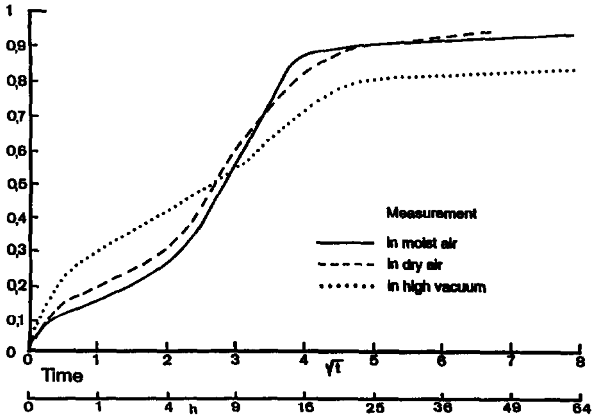


Fig. 4. Decomposition rate α_{TG} versus $\sqrt{t}$.

zinc oxide in a gaseous phase of CO_2 water vapour in a temperature range between room temperature and 200°C. This reaction is topochemical.

The adsorption of CO_2/water vapour happens rather quickly, if the oxide has not been heated over 600°C during or after the decomposition. The rate of the decomposition of the hydroxide carbonate phase mainly depends on how far the crystallites have developed to bigger particles with lower specific surface during the decomposition of the disordered domains.

The experiments showed that the decomposition rate of the hydroxide carbonate depends on the composition of the experimental atmosphere, especially on the local water vapour pressure. Zinc oxide shows no weight increase in a CO_2 atmosphere at a moisture ratio (p/p_0) below 0.1, i.e. there is no formation of hydroxide carbonate.

Above a moisture ratio of 0.35, zinc oxide absorbs in a short time more water than needed for the formation of basic carbonate. The back reaction is slower at moisture ratios from 0.1 to 0.3 and it does not normally lead to the complete stoichiometric composition of hydroxide carbonate.

The synthesis of hydroxide carbonate, with the zinc oxide cooled in a CO_2/water vapour atmosphere, starts in the adsorption layers of water in zinc oxide, into which CO_2 diffuses. The ZnO that is found in this layer, reacts with CO_2 and H_2O and develops hydroxide carbonate.

MEASUREMENTS IN CO_2 /WATER VAPOUR

A special furnace [6] was used with the thermobalance for the decomposition and back reaction experiments of the hydroxide carbonate in flowing

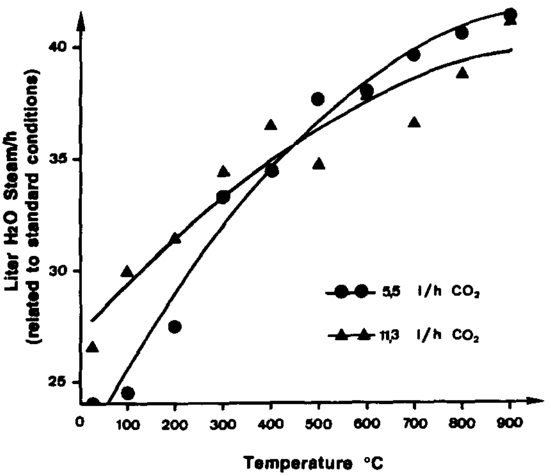


Fig. 5. Diagram showing the water vapour transport for two gas flow rates of CO_2 through the furnace of a thermobalance as a function of temperature under standard conditions (20°C and 0.1 Mpa).

gases saturated with water vapour. If the measurements are made in flowing gases, the investigated material in the crucible can react with the gases during the heating/cooling period and the flow can remove gaseous products of the sample. If gases constantly flow and are saturated with water vapour, the amount of water vapour transported will also be constant at higher isothermal conditions. The humidity changes with the temperature of the flowing gases in measurements involving a linear temperature rise. Because of this, measurements were made to determine the rate of the water vapour flow through the reaction chamber (furnace) of the balance at different temperatures. The results are shown for two different flow rates of CO_2 in Fig. 5. The curves show the water vapour flow as a function of the temperature according to the measured amounts of condensate.

CONCLUSIONS

In decomposition reactions at low temperatures (about 250°C), there are significant differences in the activation energy depending on the partial water vapour pressure of the atmosphere, i.e. depending on whether dry or moist air or vacuum is used. The reason for this is that transport processes can take place in the film of adsorbed water on crystals of the starting material, just as on the reaction product. Reaction products can, by means of such transport processes, reorganize their crystal structure, grow in size and improve their crystallinity.

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