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Investigation of the effect of intensive ball milling in a planetary ball mill on the thermal decomposition of cadmium carbonate and basic zinc carbonate

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Summary The kinetics of thermal decomposition of cadmium carbonate CdCO₃ and basic zinc carbonate ZnCO₃·nZn(OH)₂ and the effect of intensive milling in a planetary ball mill on its parameters, have been investigated. The values of the reaction heat and of the activation energies of thermal decomposition have been determined for both the compounds. Investigations of the thermal decomposition of the products of ball milling of investigated compounds revealed a slight effect of milling conditions on the reaction temperature and heat consumed during the thermal decomposition of ZnCO₃·nZn(OH)₂. No effect of ball milling on the thermal decomposition of CdCO₃ has been found.

1. Introduction
Studies of the effect of mechanical deformation on the chemical reactivity of solids, called mechanochemistry, are nowadays an important research area in the field of physical chemistry and chemistry of solids [1,2]. Mechanochemistry offers the possibility to conduct various reactions, including the synthesis of substances in the nanocrystalline and amorphous states, at low temperatures without dissolution or fusion of the reactants.

Fifty years after the pioneering works of Benjamin [3] the mechanochemical treatment of substrates in producing new thermodynamically stable and metastable materials, often non achievable by traditional methods, is well established and received industrial applications. While the method is progressing at the industrial level, knowledge about the physical mechanisms operating during the mechanochemical treatment (eg. ball milling) is still very limited due to serious difficulties in quantifying this complex process [4].

A survey of the recent literature indicated that nowadays the research effort in mechanochemistry is mainly devoted to preparation of new metastable and stable metallic materials. In the field of nonmetallic inorganic compounds the mechanically induced polymorphic phase transition in many oxides were reported. Successful syntheses of many compounds, eg. copper and silver chalcogenides, have been described, too [3,4].

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In our previous study we observed a distinct effect of ball milling on the thermal decomposition of lead carbonate PbCO$_3$ [5]. The purpose of the present study was to observe the eventual effect of ball milling on the thermal decomposition of cadmium carbonate CdCO$_3$ and basic zinc carbonate ZnCO$_3$·nZn(OH)$_2$. The existing literature data on the thermal decomposition of cadmium and zinc carbonates are very old and the values of heat and activation energy for decomposition of these compounds, reported by different authors, do not agree among themselves [6,7]. Till now the effect of mechanical deformation on the thermal decomposition of PbCO$_3$ and ZnCO$_3$·nZn(OH)$_2$ has not been investigated.

2. Experimental conditions
Chemically pure powders of cadmium carbonate CdCO$_3$ and basic zinc carbonate ZnCO$_3$·nZn(OH)$_2$, both supplied by POCh Gliwice, were used in the experiments. Thermal decomposition of starting materials, as well as of products obtained by intensive ball milling, was investigated by differential thermal analysis, performed using the NETZSCH DSC 404/3F differential scanning calorimeter with the S-type Pt-PtRh measuring head and standard platinum sample pans. An empty sample pan was used as the reference. The masses of the samples in each DSC experiment series were nearly the same (~18 mg for ZnCO$_3$·nH$_2$O and ~47 mg in the case of CdCO$_3$).

The investigated compounds were milled in a planetary ball mill Pulverisette 7 produced by FRITSCH. Milling was carried out in two grinding vials of 25 ccm volume containing balls with diameter of 12 mm. Both the vials and balls were made of stainless CrNi steel. The milling conditions were changed by changing the milling time, the number of milling balls and of the rotation speed of the planetary system of milling device.

All the milling procedures and DTA experiments were performed in atmospheric air under normal pressure.

3. Results and discussion
The DSC traces for unmilled CdCO$_3$ and ZnCO$_3$·nZn(OH)$_2$ samples, registered at the heating/cooling rate of 10 K/min, are shown on Fig.1. In the first heating run distinct endotherms, revealing the thermal decomposition of investigated compounds, were observed. On the DSC traces registered in the cooling run as well as during the second heating run (with the same sample) no thermal effects were observed. This means that the investigated carbonate samples have been completely decomposed in the first heating run.

![DSC traces for CdCO$_3$ and ZnCO$_3$·nZn(OH)$_2$](image)

Figure 1. DSC traces for CdCO$_3$ and ZnCO$_3$·nZn(OH)$_2$ registered at the heating/cooling rate of 10 K/min. 1 – first heating run, 2 - cooling run, 3 – second heating run.
This conclusion was confirmed by the observation, that the relative difference of the mass of the sample before and after the first heating-cooling run agrees well with the theoretical mass deficit caused by the thermal decomposition of investigated materials. The shape of the endotherm displayed on the DSC curve for CdCO$_3$ indicates that the thermal decomposition occurs in a single step. The endotherm observed on the DSC curve for ZnCO$_3$·nZn(OH)$_2$ consists of two mutually overlapping peaks. This suggests that the thermal decomposition of this substance occurs in two subsequent stages. Probably, the first of them corresponds to the thermolysis of less stable hydroxide component.

With increasing the heating rate the positions of DSC endotherms corresponding to the thermal decomposition of investigated compounds systematically shift towards higher temperatures (Fig. 2). This effect is typical of thermally activated processes and allows for determination of the value of activation energy.

\[
\frac{1}{T} \text{ (10^3 K)}^{-1} = \begin{array}{c|c|c}
\text{CdCO}_3 & \text{ZnCO}_3\cdot n\text{Zn(OH)}_2 \\
1.90 & 1.95 & 2.00 & 2.05 & 2.10 & 2.15 \\
1.35 & 1.40 & 1.45 & 1.50 & 1.55 & 1.60 & 1.65 \\
0.0 & 0.5 & 1.0 & 1.5 & 2.0 & 2.5 & 3.0 & 3.5
\end{array}
\]

\[
\ln \frac{v}{T} = \begin{array}{c}
-1.35 & -1.40 & -1.45 & -1.50 & -1.55 & -1.60 & -1.65 & -1.70 & -1.75
\end{array}
\]

\[
\begin{array}{c|c|c|c|c}
\text{CdCO}_3 & \text{ZnCO}_3\cdot n\text{Zn(OH)}_2 \\
20 & 10 & 5 & 20 & 10 & 5
\end{array}
\]

**Figure 2.** Exemplary DSC traces for unmilled CdCO$_3$ and ZnCO$_3$·nZn(OH)$_2$ samples registered at different heating rates. Parameter – heating rate in K/min.

\[
\frac{1}{T} \text{ (10^3 K)}^{-1} = \begin{array}{c|c|c}
\text{CdCO}_3 & \text{ZnCO}_3\cdot n\text{Zn(OH)}_2 \\
1.90 & 1.95 & 2.00 & 2.05 & 2.10 & 2.15 \\
1.35 & 1.40 & 1.45 & 1.50 & 1.55 & 1.60 & 1.65 \\
0.0 & 0.5 & 1.0 & 1.5 & 2.0 & 2.5 & 3.0 & 3.5
\end{array}
\]

**Figure 3.** Ozawa’s plots for reaction temperatures of unmilled CdCO$_3$ and ZnCO$_3$·nZn(OH)$_2$ samples. I and II denote the two subsequent stages of decomposition.
The activation energies for thermal decomposition of investigated carbonates have been determined by
the method proposed by Ozawa [8]. For this purpose the so called “Ozawa plots” \( \ln v = f(1/T) \) were
constructed (Fig. 3), where \( T \) denotes the reaction temperature determined at the heating rate \( v \).
Reaction temperatures \( T \) were determined from the intersection of tangent to the low-temperature
(left) side of endotherm with the base line of recorded DSC trace. As it is seen on Fig. 3, the data
points for reaction temperatures registered at different heating rates are located along straight lines.
The slopes of these lines multiplied by the universal gas constant \( R \) give the value of the activation
energies of investigated processes.

The obtained this way values of the activation energy for the single stage thermal decomposition of
CdCO\(_3\) and for the two stages of thermolysis of ZnCO\(_3\)\(\cdot\)nZn(OH)\(_2\) are collected, and compared with
the existing literature data, in Table 1.

### Table 1. Activation energy and reaction heat for thermal decomposition of cadmium and zinc carbonates

| Compound             | Activation energy (kJ/mole) | Reaction heat (kJ/mole) |
|----------------------|-----------------------------|-------------------------|
|                      | present work | literature data | present work | literature data |
| CdCO\(_3\)           | 175.3         | 151 [7]         | 84.3         | 99.0 [7]        |
| ZnCO\(_3\)           | 151 [7]       | 71.1 [7]        |              |                |
| ZnCO\(_3\)\(\cdot\)nZn(OH)\(_2\) | 92.7 – I stage | 127.9            |              |                |
|                      | 231.0 – II stage |                   |              |                |

The area under the peaks on the DSC traces is proportional to the heat of observed chemical
reaction or structural transformation. Making use of the calibration experiment in which the endotherm
corresponding to the melting of high purity tin was registered, the heat consumed during the thermal
decomposition of investigated cadmium and zinc carbonates has been determined. In Table I the
obtained results are collected and compared with the literature data.

An inspection of the data given in Table I indicates, that the obtained value the activation energy
for thermolysis of cadmium carbonate is higher than the values reported in literature [6, 7], and the
reaction heat is by 15 % lower than that reported in [7]. No direct comparison with literature data for
ZnCO\(_3\)\(\cdot\)nZn(OH)\(_2\) could be made. The reaction heat is obviously much higher than that for pure
ZnCO\(_3\) [7], and the activation energy for thermal decomposition of pure ZnCO\(_3\) is higher than that for
the first stage and lower than that for the second stage of thermolysis of ZnCO\(_3\)\(\cdot\)nZn(OH)\(_2\) .

With the aim to check if the milling of investigated carbonates affects their thermal decomposition,
observed by thermal analysis of milling products, two series of experiments were performed, in which
the values of the reaction heat and decomposition temperature were determined for the products of
milling carried under systematically changed milling conditions.

Figure 4 represents the dependencies of the decomposition temperature (left) and of the reaction
heat (right) on the time of milling carried with 5 balls in the milling vial at a constant rotation speed
of plate supporting the milling vial (366 m\(^{-1}\)). As it is seen, for CdCO\(_3\) the milling procedure
practically does not affect both the temperature and the decomposition heat of investigated material.
This means that milling does not cause the thermal decomposition of investigated material. In the case
of ZnCO\(_3\)\(\cdot\)nZn(OH)\(_2\) the lowering of the decomposition temperature is observed in the first 50 minutes
of milling. Further increase of the milling time does not change the decomposition temperature of
investigated cadmium carbonate. Slight, but systematic lowering of the reaction heat extending over
the whole range of milling time (0 – 300 min) is observed. This suggests, that milling causes partial
decomposition of investigated carbonate (up to ~15\%). The decomposition kinetics is probably also
slightly affected (change in the decomposition temperature), but this point deserves further systematic studies.

Next, the intensity of milling was changed by changing the rotation speed of the milling device. Figure 5 represents the effect of the rotation speed of plate supporting the milling device on the temperature (left) and heat (right) of decomposition of the milling products. In all this measurement series the milling time was 120 min and 5 balls in the milling vials were used.

As it is seen on Figure 5, the change in the rotation speed (220 – 510 min\(^{-1}\)) does not affect the decomposition temperature of both the investigated carbonates. For CdCO\(_3\) the heat of decomposition does not depend on the rotation speed of milling device. In contrast to this, the heat of decomposition of the products of milling of ZnCO\(_3\)-nZn(OH)\(_2\) systematically diminishes with increasing the rotation speed (milling intensity).

**Figure 4.** Effect of the milling time on the decomposition temperature (left) and the reaction heat (right) of the products of milling of investigated cadmium and zinc carbonates (5 balls, rotation speed of plate supporting the milling device ~ 366/min).

**Figure 5.** Effect of the rotation speed of plate supporting the milling device on the decomposition temperature (left) and on the decomposition heat (right) of the milling products of investigated cadmium and zinc carbonates (5 balls, milling time 120 min).

Concluding, it may be stated that milling does not affect the thermal decomposition of cadmium carbonate, and slightly affects the thermolysis of ZnCO\(_3\)-nZn(OH)\(_2\). This is in contrast with lead
carbonate PbCO₃, for which under comparable conditions a distinct effect of milling on the thermal decomposition has been observed [5]. The reasons for different behaviour of different carbonates during the milling process seems to be an interesting problem to be solved in further studies. First of all, the observation that ball milling affects only the thermal decomposition of carbonates decomposing in more than one stage (ZnCO₃·nZn(OH)₂ and PbCO₃) must be confirmed. With this aim we started the investigations of other carbonates decomposing in one and/or in many stages. Another factor responsible for different effect of ball milling of investigated materials on their thermal decomposition is, probably, the value of the difference of formation energies of the substrates (carbonates) and products (oxides) of thermal decomposition. Solution of this problem requires further theoretical and experimental studies.

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