Journal of Thermal Analysis and Calorimetry, Vol. 60 (2000) 59–65

THE USE OF THERMOGRAVIMETRY TO ASSESS THE EFFECT OF MECHANICAL ACTIVATION OF SELECTED INORGANIC SALTS

K. Wieczorek-Ciurowa[1], *Ju. G. Shirokov*[2] *and M. Paryło*[1]

[1]Institute of Inorganic Chemistry and Technology, Cracow University of Technology, Warszawska 24
31-155 Cracow, Poland
[2]Ivanovo State Academy of Chemistry and Technology, Engels Prospect 7, 153-460 Ivanovo, Russia

Abstract

The thermal decomposition of malachite and calcite and their physical mixture was studied by thermogravimetry employed as a tool for the estimation of physicochemical changes in solids, caused by dry grinding. For the identification of solids X-ray powder diffraction and IR spectroscopy were used.

Keywords: calcite, catalysts, grinding, malachite, mechanical activation, phase analysis, thermogravimetry

Introduction

Mechanical activation of solids by dry grinding and intimate mixing of heterogeneous materials can be a stage in the preparation of mixed catalysts. Thus, activation of solids at ambient temperature exemplified by hydroxocarbonates of some bivalent elements (Cu, Mn, Co, Ti, Ni) leads to changes in their physical and chemical properties. These kind of compounds, after ‘intensive’ grinding for several minutes, may pass to an amorphous form and finally decompose to oxides. Moreover, an increase of chemical reaction rate between the components of the system is possible, with the formation of new compounds [1–7].

Phase transformations and changes in crystalline structure in mechanically activated solids can be examined by X-ray powder diffraction, IR spectroscopy, thermal analysis and other physicochemical methods of analysis. However, only thermoanalytical techniques are universal in this case because they offer the possibility of identifying highly defected or finely crystalline phases, which might be difficult by X-ray diffraction methods. Characteristic thermal effects are preserved for the above compounds but departures from the structure of the untreated parent solid may influence the temperature of chemical processes, their enthalpy and/or kinetics of transformations.

The aim of this research was to illustrate the use of thermogravimetry for estimating changes in the physicochemical properties of mechanically activated two-component

1418–2874/2000/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

mixture of salts. The salts used in the study were malachite, $Cu_2(OH)_2CO_3$, and calcite, $CaCO_3$.

Experimental

Materials

Malachite, $Cu_2(OH)_2CO_3$, and calcite, $CaCO_3$, the materials to be activated by mechanical treatment (dry grinding) were obtained by precipitation from aqueous solutions. The system of malachite and calcite was prepared as a physical mixture at a molar ratio of CuO/CaO=1.

Mechanical grinding was carried out for 5, 10 and 15 min in air at ambient temperature. A planetary mill, was employed with an energy consumption of 135.0 kW kg^{-1}, as described in detail previously [8].

The following notation is introduced in the paper:

A0 – malachite untreated; A5, A10 and A15 – activated for 5, 10 and 15 min, respectively; B0 – calcite; AB0, AB5, AB10 and AB15 – mixture of malachite (A0) and calcite (B0) – activated for 0, 5, 10 and 15 min, respectively.

Equipment and methods of measurement

Thermogravimetric analyses (TG/DTG curves) of the samples were carried out on a Mettler thermobalance TG-50 in a Mettler TA-4000 System. Records were obtained with samples heated at a rate of 24°C min^{-1}, up to 950°C, in an open platinum crucible. The sample size was about 20 mg.

X-ray powder diffraction patterns were obtained using a Philips X'Pert Diffractometer (CuK_α) in the 2Θ range of 10–60°.

The IR spectra in the region of 4000–400 cm^{-1} were recorded by means of UR-20 Spectrometer (Zeiss Jena) using KBr pellets.

Results and discussion

The TG and DTG sets of curves for mechanically activated and untreated malachite, $Cu_2(OH)_2CO_3$, are shown in Fig. 1. Under given experimental conditions, the decomposition of all malachite samples (A0, A5, A10 and A15) is effected between 150 and 400°C in two completely overlapping stages. The mass loss corresponds to the evolution of water (from the OH groups bound in the malachite lattice) and CO_2 yielding CuO as a final solid product according to the reaction:

$$Cu_2(OH)_2CO_3 \rightarrow 2CuO + H_2O + CO_2$$

Theoretical malachite composition (%) is: CuO – 72.0, H_2O – 8.1 and CO_2 – 19.9.

The smaller effect of mass loss which appears at lower temperatures, i.e. below 150°C, only in cases of activated samples (A5, A10 and A15) is due to the escape of

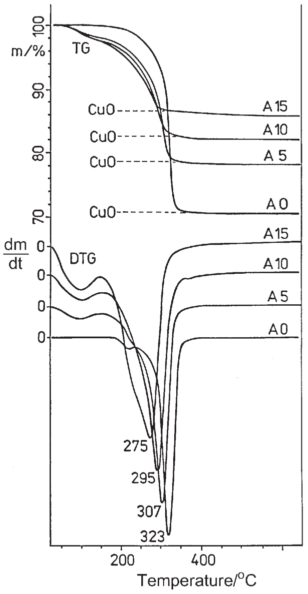

Fig. 1 The compiled TG and DTG curves for malachite samples: A0 – untreated; A5, A10 and A15 – after grinding for 5, 10 and 15 min, respectively (the original DTG curves for A0, A5, A10 and A15 samples had vertical scales in the ratios: 1:0.4:0.3:0.2, respectively)

molecules of water formed during the grinding of malachite and remained in the solid samples.

Table 1 Degree of decomposition of malachite (A0) and product composition of mechanically activated malachite during different time

Sample	Activation time/min	Composition/%			Degree of $Cu_2(OH)_2CO_3$ decomposition/%
		$H_2O_{(l)}$	$CuO_{(s)}$	$Cu_2(OH)_2CO_{3(s)}$	
A0	0	<1	0	99.0	0
A5	5	2.0	27.0	71.0	35
A10	10	2.5	42.0	55.0	51
A15	15	2.7	56.0	41.3	65

The influence of the grinding time on the actual composition of activated malachite and the degree of conversion of malachite to CuO is presented in Table 1. An increase in the amount of CuO and a decrease in the proportion of malachite determined from TG/DTG curves after dry grinding are confirmed by X-ray data shown in Fig. 2. Moreover, it is evident that CuO is crystalline and the remaining malachite is amorphous. This is also confirmed by comparing IR bands for A0 and A15 samples in Fig. 3. Differences in the water content (adsorbed and constitutional) from malachite are also detected by IR absorption spectra of A0 and A15 samples.

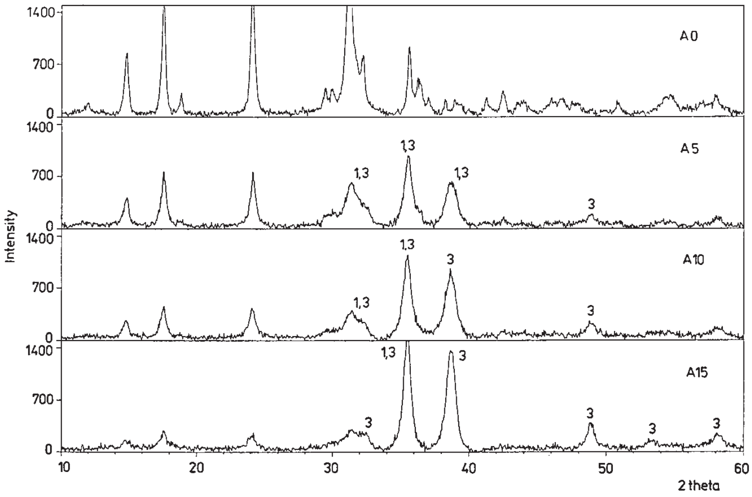

Fig. 2 X-ray diffraction patterns for malachite samples: A0 – untreated, A5, A10 and A15 – after grinding for 5, 10 and 15 min, respectively. 1 – malachite; 3 – CuO

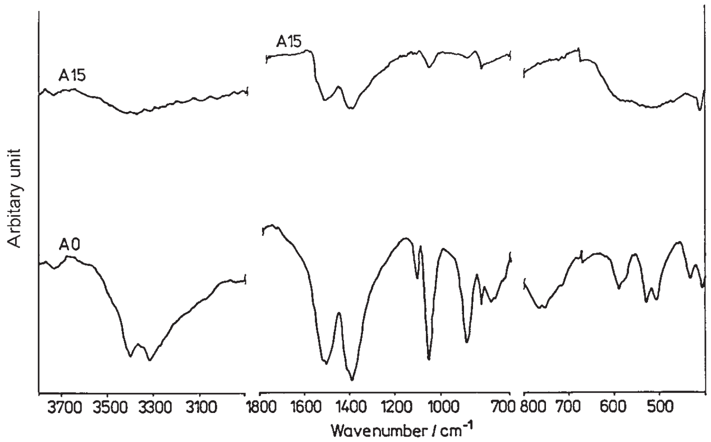

Fig. 3 IR spectra for malachite samples: A0 – untreated, A15 – after grinding for 15 min

An appreciable decrease in the decomposition temperature of malachite samples after grinding is observed from 323 to 275°C. It is obvious that the mechanical activation greatly accelerated the decomposition of $Cu_2(OH)_2CO_3$ because of the breaking up of crystallites and the production of new surface.

In the case of calcite, samples activated under similar conditions subjected to thermogravimetric analysis are not affected in the same way, which reflects the thermal stability of $CaCO_3$ (the TG/DTG curves are not presented here). This is independent of the time of grinding. The sole effect of the grinding is an increase in the amount of adsorbed (hygroscopic) water.

Table 2 Degree of decomposition of malachite and product composition of mechanically activated mixture of malachite and calcite during different time

Sample	Activation time/min	Composition/%				Degree of $Cu_2(OH)_2CO_3$ decomposition/%
		$H_2O_{(l)}$	$Cu_2(OH)_2CO_{3(s)}$	$CaCO_{3(s)}$	$CuO_{(s)}$	
AB0	0	1	53.0	46.0 (0)*	0	0
AB5	5	2.0	24.0	49.0 (1.0)*	25.0	59
AB10	10	2.5	14.0	51.0 (2.0)*	35.5	77
AB15	15	1.8	5.7	53.0 (3.0)*	39.5	91

* The numbers in brackets correspond to the amount of $CaCO_3$ as aragonite, not calcite

Grinding of malachite and calcite mixture during 15 min brings near total decomposition of malachite to CuO, as is illustrated by TG/DTG curves in Fig. 4. Degree of the decomposition of samples ground with calcite is appreciably higher that of malachite ground alone (compare Tables 1 and 2). The calcite appears to play the part of an abrasive. The calcium carbonate remains undecomposed, however partial polymorphic transformation to aragonite takes place. At the same time the degree of crystallinity of calcite decreases, which is illustrating by the X-ray diffraction patterns in Fig. 5. There is no chemical interaction between calcium carbonate and malachite.

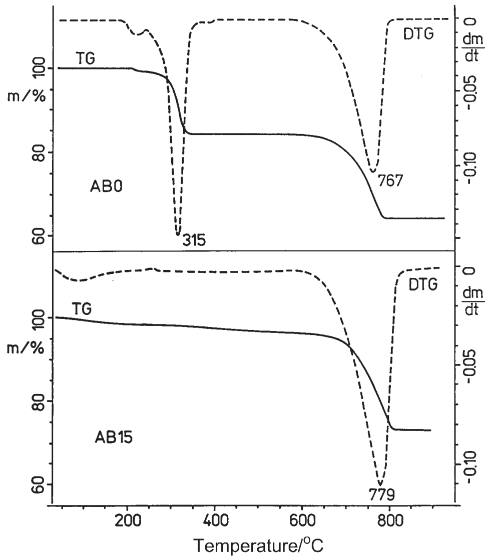

Fig. 4 Two sets of TG/DTG curves for mixture of $Cu_2(OH)_2CO_3$ and $CaCO_3$ samples: AB0 – untreated, AB15 – after grinding for 15 min

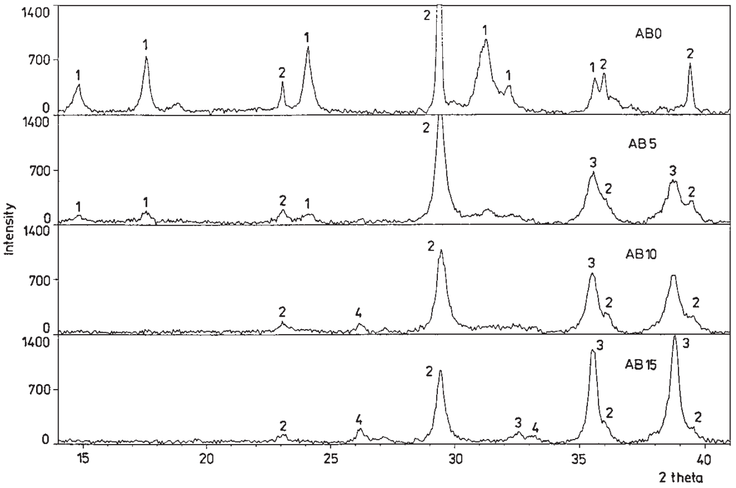

Fig. 5 X-ray diffraction patterns for mixture of $Cu_2(OH)_2CO_3$ and $CaCO_3$ (CuO:CaO=1) samples after mechanical treatment: AB0 – untreated, AB5, AB10 and AB15 – ground for 5, 10 and 15 min, respectively 1 – malachite, 2 – $CaCO_3$ (calcite), 3 – CuO, 4 – $CaCO_3$ (aragonite)

Conclusions

1. The loss of water and carbon dioxide for malachite samples untreated and after mechanical activation by grinding was quantified on the basis of TG/DTG curves. The proportion of malachite, $Cu_2(OH)_2CO_3$, decomposing during heating in thermobalance was calculated. From the measured total amount of CuO (the only final product), the original mass of malachite present could be determined.
2. The procedure used for the quantitative determination of carbon dioxide and water is applicable to both – simple substances and mixtures of carbonates and hydroxocarbonates subjected to mechanical treatment.

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The authors wishes to thank Dr. W Balcerowiak at the Institute of Heavy Organic Synthesis in Kędzierzyn-Koźle for his help in the thermoanalytical measurements. This work was supported by the Polish State Committee for Scientific Research (KBN), grant C-1/53/DS/98.

References

1 V. V. Boldyrev, Kinetics and Catalysis, 13 (1972) 1411 (in Russian).
2 P. G. Fox, J. Materials Science, 10 (1975) 340.
3 J. G. Avvakumov, Mechanochemical activation methods in chemical processes, Novosibirsk, Nauka 1986, p. 306 (in Russian).
4 P. J. Butyagin, Kinetics and Catalysis, 28 (1987) 5 (in Russian).

5 Ju. G. Shirokov, V. J. Prokofev, N. N. Smirnov and K. Wieczorek-Ciurowa, Czasopismo Techn., Ed. Polit. Krak., Z.3-Ch (1998) 184 (in Polish).
6 I. J. Lin, J. Thermal Anal. Cal., 52 (1998) 453.
7 A. S. Kheifets, J. Thermal Anal. Cal., 52 (1998) 463.
8 K. Wieczorek-Ciurowa, M. Paryło and Ju. G. Shirokov, Czasopismo Techn., Ed. Polit. Krak., Z.3-Ch (1999) 67 (in Polish).