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PREPARATION AND THERMAL ANALYSIS OF SYNTHETIC MALACHITE $CuCO_3 \cdot Cu(OH)_2$

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The synthesis of malachite $CuCO_3 \cdot Cu(OH)_2$ or $Cu_2CO_3(OH)_2$ was studied through titrations of copper(II) salt solutions with a solution of sodium carbonate at different temperatures. The precipitates were characterized by TG, IR and chemical analysis. The composition varies depending on the *pH* of the solution and the temperature. Purer malachite was synthesized by simple mixing of a solution of copper(II) nitrate or sulfate with a solution of sodium carbonate at 50°C.

The kinetics of the thermal decomposition of synthetic malachite was described by either R_3 or $A_m(m=1.2–1.4)$ law, according to TG analysis, both isothermal and nonisothermal. The Arrhenius parameters determined using three different integral methods showed the kinetic compensation effect, which is correlated to the working temperature interval analyzed.

Keywords: kinetics of thermal decomposition, synthetic malachite

Introduction

Pure $CuCO_3 \cdot Cu(OH)_2$ is synthesized by mixing 0.1 *M* copper(II) salt solution with 0.1 *M*-Na_2CO_3 solution at 50°C in a mole ratio of 1.0 or with a little excess of Na_2CO_3. Formation of synthetic malachite was examined comprehensively through titrations, normal and reverse, under various experimental conditions. Kinetic analysis by thermogravimetry, both isothermal and nonisothermal, revealed that the decomposition of synthetic malachite is regulated by either $R_n(n=3)$ or $A_m(m=1.2–1.4)$ law. The Arrhenius parameters determined using three different methods showed the kinetic compensation effect, which is rationalized in view of the working temperature interval analyzed.

It is known that copper(II) carbonate hydroxide, or synthetic malachite is obtained by reacting a solution of copper(II) nitrate with a solution containing the equivalent amount of sodium carbonate at room temperature [1]. However, little

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is reported on the condition for preparing pure synthetic malachite from solution, and chemistry of the formation of synthetic malachite in solution is unsolved. There is some discrepancy about the composition reported earlier, in spite of the known reaction:

$$2Cu^{2+}+2CO_3^{2-}+H_2O \rightarrow CuCO_3 \cdot Cu(OH)_2+CO_2$$

It is thus worth studying the above reactions through titration as well as by mixing the two solutions under various experimental conditions. It also seems interesting to investigate thermal decomposition of synthetic malachite which proceeds in a single step to give copper(II) oxide [2, 3]. Thermogravimetry is to be useful in confirming the composition as well as in analyzing the kinetics of the thermal decomposition. It is hoped that such a thermal analysis of the precipitates prepared under different experimental conditions is suitable as an undergraduate thermal analysis experiment [4].

Experimental

A copper(II) salt solution was reacted with a solution of Na_2CO_3 by mixing as well as by titration under the various experimental conditions. Both normal and reverse titrations were performed. As the copper(II) salt, were used copper(II) nitrate, copper(II) sulfate and copper(II) acetate. The precipitates were separated after ageing for some time in the solution, washed with water and dried at 75°C. Table 1 summarizes the reactions examined in the present study. The solid products were characterized by IR spectroscopy, X-ray diffractometry, chemical analysis and TG-DSC. TG measurements were carried out on a Shimadzu thermobalance TGA-50 system. DSC curves were recorded on a Rigaku Thermoflex TG-DSC 8085E1 system with a sample size of 12–18 mg in a nitrogen flow at a flow rate of 30 ml/min.

Kinetic analyses of the isothermal and nonisothermal decompositions of synthetic malachite were made using a Shimadzu Thermobalance Model TGA-50 with a sample size of ca. 2 mg in a nitogen flow at a flow rate of 30 ml/min.

Results and discussion

Reaction of a $Cu(NO_3)_2$ solution with a Na_2CO_3 solution

(a) Precipitates obtained by simple mixing. Table 1 shows the results of TG analysis and determination of Cu^{2+} in various products. Samples A_{25} and A_{50} appear to be synthetic malachite and this was confirmed by TG-DSC, IR spectroscopy [5] and X-ray diffractometry [6]. The typical TG-DSC curves are shown in Fig. 1. The similar result was obtained for Samples B_{25} and B_{50}.

(b) Precipitates obtained by titration. Figure 2 shows typical titration curves (a) and (b) for the titration of 0.1 M-$Cu(NO_3)_2$ solution with 0.1 M-Na_2CO_3 solution and the reverse titration at 25°C, respectively. In view of the inflection point at the mole ratio of Na_2CO_3 to $Cu(NO_3)_2$=1.0, Sample a_{25} may be synthetic malachite, $CuCO_3 \cdot Cu(OH)_2$. According to TG and chemical analysis, however, it seemed to contain basic copper(II) nitrate $Cu(NO_3)_2 \cdot 3Cu(OH)_2$, other than basic copper(II) carbonate. This was also supported by their IR spectra. Formation of basic copper(II) nitrate was also reported for titration of 0.5 M-$Cu(NO_3)_2$ solution with 0.5 M-Na_2CO_3 solution [7].

Table 1 The condition for the precipitations, determination of copper(II) ion in the precipitates and the mass loss due to their thermal decompositions

Reactant (Molar ratio)[a]	Temp./°C	Symbol[b]	Cu^{2+}/%[c]	Mass loss/%[d]
$Cu(NO_3)_2$+Na_2CO_3(1.0:1.0)	25	a_{25}	52.56	31.60
$Cu(NO_3)_2$+Na_2CO_3(1.0:1.3)	25	a'_{25}	55.78	29.32
Na_2CO_3+$Cu(NO_3)_2$(1.0:1.0)	25	b_{25}	49.38	28.26
$Cu(NO_3)_2$+Na_2CO_3(1.0:1.0)	25	A_{25}	54.21	28.42
$Cu(NO_3)_2$+Na_2CO_3(1.0:1.0)	50	A_{50}	55.60	28.82
Na_2CO_3+$Cu(NO_3)_2$(1.0:1.0)	25	B_{25}	55.70	27.79
Na_2CO_3+$Cu(NO_3)_2$(1.0:1.0)	50	B_{50}	56.97	27.74
$CuSO_4$+Na_2CO_3(1.0:1.3)	25	c_{25}	56.98	29.87
$CuSO_4$+Na_2CO_3(1.0:0.75)	50	c_{50}	56.54	24.24
Na_2CO_3+$CuSO_4$(1.0:1.2)	25	d_{25}	56.82	28.15
Na_2CO_3+$CuSO_4$(1.0:1.4)	50	d_{50}	56.80	24.67
$CuSO_4$+Na_2CO_3(1.0:1.0)	25	C_{25}	56.78	28.87
$CuSO_4$+Na_2CO_3(1.0:1.0)	50	C_{50}	56.68	29.17
Na_2CO_3+$CuSO_4$(1.0:1.0)	25	D_{25}	56.02	28.21
Na_2CO_3+$CuSO_4$(1.0:1.0)	50	D_{50}	55.98	29.03

a) X+Y refers to the reaction by adding Y to X and vice versa

b) Small and large letters denote the reactions by titration and simple mixing, respectively

c), d) The calculated values for $CuCO_3 \cdot Cu(OH)_2$ are 57.48 and 28.04, respectively

On the other hand, it is likely that Sample a'_{25}, which was separated from the solution at the mole ratio of Na_2CO_3 to $Cu(NO_3)_2$=1.3 is approximately synthetic malachite. This suggests that basic copper(II) nitrate may change into synthetic malachite in the solution containing an excess of Na_2CO_3. The precipitate ob-

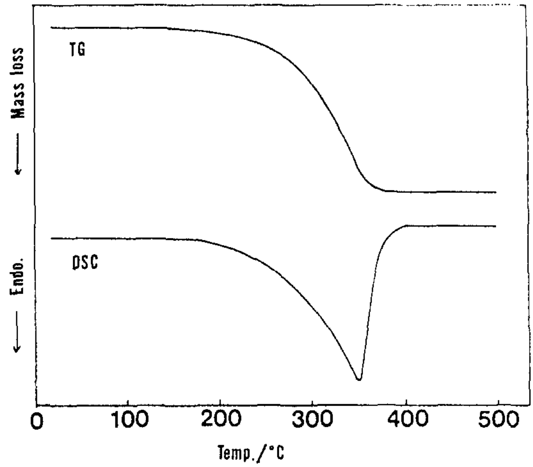

Fig. 1 TG-DSC curves for the thermal decomposition of synthetic malachite A_{50}

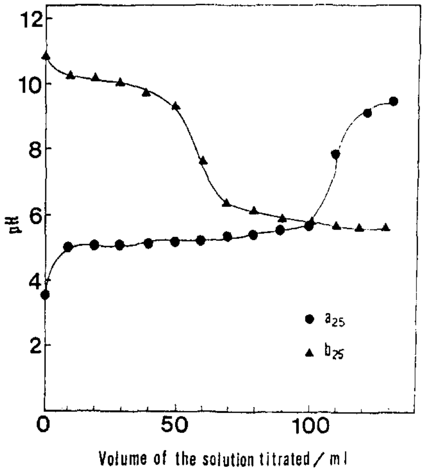

Fig. 2 Typical titration curves (a) and (b) for the titration of 0.1 *M*-$Cu(NO_3)_2$ solution with 0.1 *M*-Na_2CO_3 solution and the reverse titration at 25°C, respectively

tained by the back titration at the mole ratio of Na_2CO_3 to $Cu(NO_3)_2$ of 0.5 could be copper(II) hydroxide gel in view of the colour of the precipitate. It is likely that the copper(II) hydroxide gel reacts, at least in part, with an excess of $Cu(NO_3)_2$ solution to give Sample b_{25}, which seems to be a mixture of basic copper(II) nitrate and the copper(II) hydroxide gel unreacted.

Reaction of a $CuSO_4$ solution with a Na_2CO_3 solution

(a) Precipitates obtained by simple mixing. Samples C_{25} and C_{50} correspond in composition to synthetic malachite, as estimated from Table 2. On the other hand, it was revealed by TG that Samples D_{25} and D_{50} which were obtained by adding a $CuSO_4$ solution to a Na_2CO_3 solution contain a small amount of basic copper(II) sulfate other than synthetic malachite. It is noted here that pure synthetic malachite is obtained if 0.2 M of $CuSO_4$ is added to 0.2 M of Na_2CO_3 solutions [8]. A little excess of Na_2CO_3 is favorable for this formation of synthetic malachite on mixing a $CuSO_4$ solution with a Na_2CO_3 solution but defficiency of Na_2CO_3 tends to yield synthetic brochantite.

(b) Precipitates obtained by titration. According to the titration curves, Sample c_{25} was inferred to be synthetic malachite. However, it was found by TG that sample c_{25} contains a small amount of basic copper(II) sulfate, $CuSO_4{\cdot}3Cu(OH)_2$ which loses SO_3 at about 700°C [4]. It was shown by TG, chemical analysis and IR spectroscopy, on the other hand, that Sample c_{50} is exclusively basic copper(II) sulfate $CuSO_4{\cdot}3Cu(OH)_2$. It proved by TG and chemical analysis, that Sample d_{25} is synthetic malachite contaminated with basic copper(II) sulfate whereas Sample d_{50} is exclusively basic copper(II) sulfate.

Table 2 The relationship between the fractional reaction α and the time t(min) at various temperatures according to isothermal TG

	α			k/s^{-1}	
Temp./°C	0.1	0.5	0.9	$A_{1.4}$	$R_{3.4}$
260	54.27	404.4	1027	4.91×10^{-5}	1.03×10^{-5}
280	18.67	134.1	359.2	1.43×10^{-4}	2.96×10^{-5}
300	6.52	36.08	105.4	5.05×10^{-4}	9.99×10^{-5}
320	5.72	14.27	29.71	2.09×10^{-3}	4.35×10^{-4}

Kinetics of the thermal decomposition of synthetic malachite

(a) Isothermal analysis

It is known that synthetic malachite decomposes thermally in a single step as follows [2].

$$CuCO_3{\cdot}Cu(OH)_2 \rightarrow 2CuO+CO_2+H_2O \qquad (1)$$

Table 2 lists the relationship between the fractional reaction α and the time t at various temperatures determined from the isothermal mass loss measurements. The kinetic obedience was estimated as the R_3 law according to plots of various kinetic functions $F(\alpha)$ against t [9], when integral values of the exponents in the $F(\alpha)$ functions were used over the temperature range of 260°–320°C. When the exponents were extended to nonintegral values for the kinetic laws of A_m and R_n either $A_{1.4}$ or $R_{3.4}$ law was determined as appropriate [10]. In Table 2 are also given the rate constants k which were calculated in terms of the appropriate functions, $A_{1.4}$ and $R_{3.4}$. Table 3 shows Arrhenius parameters calculated from the Arrhenius plot.

(b) Nonisothermal analysis

Table 4 lists the relationship between the values and temperatures at various heating rates determined from TG. According to the Ozawa method of kinetic analysis [11–13], the averaged activation energy E within an α range of 0.05–0.95 was calculated as 235 kJ/mol. The kinetics of the nonisothermal dehydration was determined as regulated by the $A_{1.2}$ law with log A=17.4 1/s from the $F(\alpha)$ *vs.* Θ plot [11–13]. The fact that the E value obtained by use of the Ozawa method is larger than that obtained isothermally is explained by the so-called kinetic compensation effect [14, 15].

According to the CR method [16, 17], the D_1 law was estimated as appropriate, yielding E=220–266 kJ/mol and log A=17–20 1/s, depending on the heating

Table 3 The activation energy E and the logarithmic pre-exponential factor log A determined for the isothermal decomposition of synthetic malachite

$F(\alpha)$	E/kJ·mol^{-1}	log A/s^{-1}
$A_{1.4}$	164.2	11.7
$R_{3.4}$	163.1	10.9

Table 4 The relationship between the fractional reaction and the temperature (°C), and the Arrhenius parameters determined, by use of Coats and Redfern's method in terms of the $A_{1.4}$ law assessed isothermally, for the nonisothermal decomposition of synthetic malachite

Heating rate, deg·min^{-1}	Fractional reaction α			E/kJ·mol^{-1}	log$A$/s^{-1}	$T_H T_L/\Delta T$*
	0.1	0.5	0.9			
0.50	278.5	316.8	332.7	210	15.3	1721
1.00	287.8	326.5	341.6	223	16.4	1830
2.50	298.6	332.1	346.7	254	19.3	2162
5.04	306.8	347.1	362.2	233	17.3	2021
10.0	314.2	352.7	368.1	244	18.4	2140

* T_H and T_L are the temperatures at α=0.1 and α=0.9 at each heating rate, respectively and ΔT is the difference between T_H and T_L

rate. When the same law as for the isothermal reaction, the $A_{1.4}$ law, was assumed, quite different Arrhenius parameters as listed in Table 4 were obtained. It is noted here that the Arrhenius parameters do not decrease with the increasing heating rate. This is explained by changes in the working temperature as well as in the temperature interval [14, 15]. It is noted that the value of $T_H T_L/\Delta T$ given in the last column of Table 4 is a measure of size of E and log A [18].

* * *

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Zusammenfassung — Mittels der Titration von Kupfer(II)-salzlösungen mit einer Natriumcarbonatlösung bei verschiedenen Temperaturen wurde die Synthese von Malachit $CuCO_3Cu(OH)_2$ bzw. $Cu_2CO_3Cu(OH)_2$ untersucht. Die Niederschläge wurden mittels TG, IR und Elementaranalyse beschrieben. Die Zusammensetzung ändert sich mit dem *pH*-Wert der Lösung und der Temperatur.Ein reineres Malachit erhält man bei einfachem Vermengen einer Lösung von Kupfer(II)-nitrat oder -sulfat mit einer Natriumcarbonatlösung bei 50°C.

Die Kinetik der thermischen Zersetzung von synthetischem Malachit wurde entsprechend der TG-Analyse (sowohl isotherm als auch nichtisotherm) entweder durch das R_3- oder das A_m-Gesetz (m=1.2-1.4) beschrieben. Die unter Zuhilfenahme von drei verschiedenen Integrationsmethoden ermittelten Arrheniusschen Parameter zeigten den kinetischen Kompensationseffekt, der auf den untersuchten Arbeitstemperaturbereich bezogen wurde.