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Rheology phase reaction synthesis and thermal decomposition of magnesium phthalate dihydrate

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Abstract

Magnesium phthalate dihydrate was synthesized by rheological phase reaction. The crystal structure was determined by XRD. Its thermal decomposition mechanism in N_2 was studied by TG DTA. The thermal decomposition products were characterized by XRD, GC–MS. The thermal decomposition of magnesium phthalate dihydrate in N_2 proceeded in two stages; it first lost two crystal water to form anhydrate salt, then magnesium phthalate decomposed further, the last product was MgO. The organic compounds are mainly benzophenone and anthraquinone.

Keywords: Crystal structure; Phthalate; Rheological phase reaction; Thermal decomposition; Magnesium

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1. Introduction

There have been a lot of reports about study on phthalate so far. The thermal behavior of transition metal and rare-earth phthalate in air has been reported by Brzyska et al. [1–7]. The study on alkali-earth metal phthalate is mainly about its spectral property and crystal structure [8]. However, no detailed study has been reported on the thermal decomposition reaction mechanism of alkali-earth metal phthalate in inert atmosphere.

In this paper, we synthesized magnesium phthalate by the rheology phase reaction method and studied its crystal structure by XRD. The thermal decomposition mechanism was investigated in inert atmosphere. The products of thermal decomposition are characterized. By the thermal decomposition of magnesium phthalate dihydrate in nitrogen atmosphere, we can get some important organic product such as benzophenone and 9,10-anthaquinone. A more interesting thing is that we have obtained nanoscale magnesium oxide powder, which is widely used due to its unique physicochemical property.

The rheology phase reaction method is a process of preparing compounds or materials from a solid–liquid rheological mixture. The solid reactants were fully mixed in the proper molar ratio, and made up by adding a proper amount of water or other solvents to a solid–liquid rheological body in which the solid particles and liquid substances were uniformly distributed. After reaction under suitable experimental conditions (temperature commonly 80–100 °C), the product was obtained. There are many advantages in the rheological phase system: the surface area of solid particle can be efficiently utilized, the contact between solid particle and fluid is close and uniform, and heat exchange is very good. Local overheating can be avoided, and the reaction temperature is easy to control. In addition, many substances exhibit new reaction properties in this state.

2. Experimental

Preparation of samples. The phthalic acid and magnesium oxide are of analytical reagent grade. The phthalic acid and

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magnesium oxide were fully mixed by grinding in 1:1 molar ratio (each one is 0.05 mol), about 5 ml water was added, and prepared to the solid–liquid rheological state. Then the mixture was reacted for 14 h at about 100 °C. Magnesium phthalate was obtained by drying at 120 °C after washing with ethanol.

The contents of C, H and Mg were determined with a Perkin-Elmer 240B analyzer and by the use of EDTA titration, respectively. Elemental analysis found (calculated): C, 41.05% (42.86%); H, 3.94% (3.57%); Mg, 10.52% (10.71%).

The X-ray diffraction patterns were obtained with a Shimadzu XRD-6000 model X-ray diffractometer with a Ni-filter and graphite monochromator, and Cu $K\alpha_1$ radiation ($\lambda = 1.54056$ Å). The TG and DTA (3–5 mg sample) curves of $MgPht{\cdot}2H_2O$ were recorded with a Shimadzu DT-40 thermal analyzer in nitrogen (flow rate 50 ml min^{-1}) at a heating rate of 20 °C min^{-1} from room temperature to 900 °C.

The collection of pyrolysis products: the sample was pyrolyzed by employing the apparatus shown in the literature [9] in nitrogen at 350 and 500 °C for 2 h, respectively. The condensate of gas phase products was collected. Carbon dioxide was determined with $Ca(OH)_2$ solution.

The GC–MS analysis was carried out with Trace MS plus-Trace GC model gas chromatography–mass spectrometer (America J&W Science Company). DB-5MS elastic quartz capillary column (0.25 mm in inside diameter and 30 m in length). Gas chromatography: the carrier gas was He, pre-column pressure18 kg/m^2, starting temperature 80 °C, heating rate 10 °C min^{-1},final temperature 250 °C, gasification temperature 220 °C. Mass spectrometry: ionization manner was EI, ion source temperature 200 °C, accelerating voltage 6 kV, electron energy 70 eV, and scanning range 30–450*m*/*z*.

3. Results and discussion

The powder X-ray diffraction data of MgPht is listed in Table 1. The results indicated that the crystal structure of MgPht is monoclinic. The calculated lattice parameters are $a = 0.614$ nm, $b = 1.378$ nm, $c = 0.457$ nm, $\beta = 115.443°$, $V = 0.349$ nm^3. The intensity of diffraction peak in (0 1 0) plane is far stronger than the second stronger diffraction peak. It indicated that the structure of magnesium phthalate is layered. Magnesium ions located in the (0 1 0) plane and the benzene ring is situated on two sides of the magnesium ion plane.

Figs. 1 and 2 show the TG and DTA curves of $MgPht{\cdot}2H_2O$ in nitrogen. It can be seen that the thermal decomposition proceeded in two stages. In the first stage (132–345 °C), two crystal water lost to yield anhydrous salt. Then the anhydrous salt was decomposed. The solid residue was grayish powder. The loss in mass is 16.53%, 65.85%, respectively, in agreement with the calculated value (16.07%, 66.07%).

Table 1
Powder X-ray diffraction data of MgPht[a]

2θ (°)	d_{exp} (nm)	I/I_1	d_{calc} (nm)	*h*	*k*	*l*
6.377	13.84788	100	13.77613	0	1	0
17.221	5.14502	8	5.14042	1	1	0
20.556	4.31721	9	4.31459	1	0	−1
			4.31724	0	2	0
21.560	4.11839	12	4.12662	0	0	1
			4.11738	1	1	−1
24.284	3.66209	<1	3.65649	1	2	−1
25.128	3.54100	6	3.54996	0	2	1
			3.53557	1	3	0
25.845	3.44444	5	3.44403	0	4	0
29.040	3.07226	2	3.06936	0	3	1
30.154	2.96131	17	2.96532	2	0	−1
32.282	2.77073	2	2.77029	2	0	0
32.871	2.72249	2	2.71592	2	1	0
			2.72226	2	2	−1
33.861	2.64505	2	2.64415	0	4	1
37.767	2.38001	2	2.38161	1	3	1
41.710	2.16368	6	2.16480	1	2	−2
			2.15862	2	4	0
			2.16581	1	4	1
43.855	2.06271	<1	2.06331	0	0	2
45.187	2.00496	<1	2.00637	0	6	1
46.332	1.95801	3	1.95887	1	5	1
			1.95354	2	5	0
			1.96027	3	2	−1
48.706	1.86799	<1	1.86799	3	3	−1

[a] Monolinic: $a = 0.614$ nm, $b = 1.378$ nm, $c = 0.457$ nm, $\beta = 115.443°$, $V = 0.349$ nm^3.

An interesting fact is that three endothermic peaks were observed in Fig. 2. Obviously, the first one is water-lost peak. The decomposition reaction corresponding to the second peak has not finished, another reaction followed at about 540 °C. That means two reactions are corresponding to the third peak. The first reaction finished earlier than the second one. As a result, the third broad endothermic peak appears in DTA curve. There is no obvious limit between the two reactions, so one-step mass loss is shown in TG curve.

When $MgPht{\cdot}2H_2O$ was decomposed at 350 °C in nitrogen, water detected was the condensate of the gas phase product. When the sample was decomposed at 500 °C in

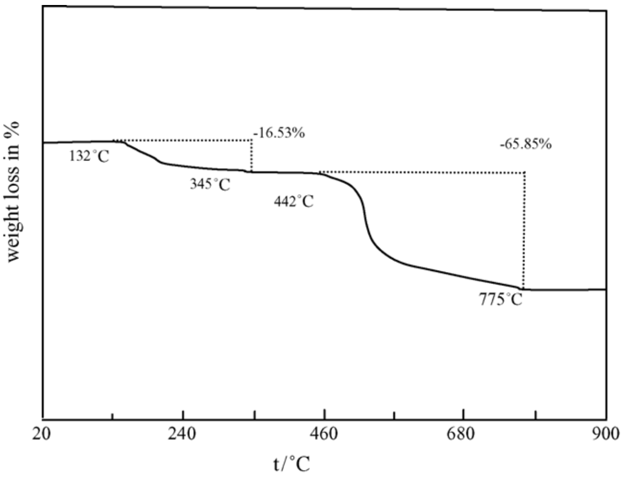


Fig. 1. TG curve of $MgPht{\cdot}2H_2O$.

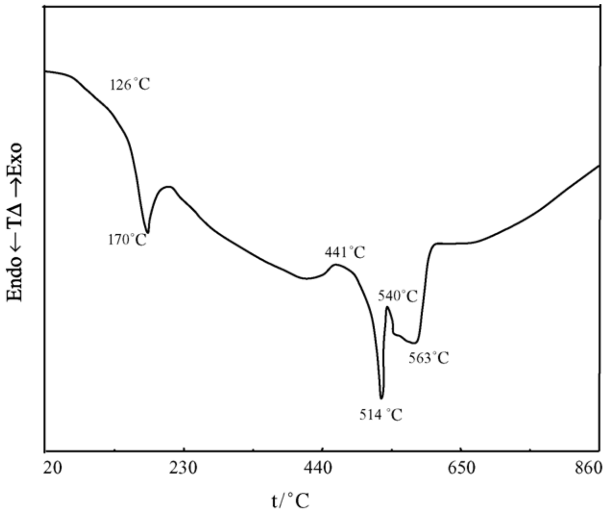


Fig. 2. DTA curve of MgPht·$2H_2O$.

nitrogen, CO_2 was detected in the gas products by means of a chemical method. The condensate of the gas phase product is dark brown and sticky oily matter. The results of GC–MS analysis are presented in Table 2.

It is shown in Table 2 that the condensate of gas phase products of the decomposition of MgPht·H_2O at 500 °C in nitrogen is mainly benzophenone and 9,10-anthaquinone.

The solid product of thermal decomposition of MgPht·$2H_2O$ at 750 °C in nitrogen atmosphere is grayish powder. It is probably containing a little black carbon. The X-ray powder diffraction graph is shown in Fig. 3. The reflections are in agreement with that of magnesium oxide of periclase (JCPDS card 43-1022). The cell parameters were calculated from XRD data. It is cubic, $a = 4.213$ nm. By calculating with line-width method, the particle size of magnesium oxide is about 11 nm.

The above results revealed the thermal decomposition mechanism as follows:

During the thermal decomposition of magnesium phthalate, the fracture of bond occurred chiefly in accordance with Eqs. (1) and (2), to form the two radicals $^\bullet C_6H_4C(O)^\bullet$ and $:C_6H_4$.

Table 2
GC–MS result of condensate of gas phase products for the thermal decomposition of MgPht·$2H_2O$ at 500 °C in nitrogen

No.	Retention time (min)	Molecular weight	Compound	Peak area (%)
1	9.73	168	Diphenylmethane	0.27
2	11.68	166	Fluorene	0.73
3	12.19	182	Benzophenone	15.88
4	13.47	180	Fluorenone	7.16
5	15.95	208	9,10-Anthraquinone	19.80
6	16.09	244	Triphenylmethane	0.54
7	17.47	242	9-Phenylpluorene	2.57

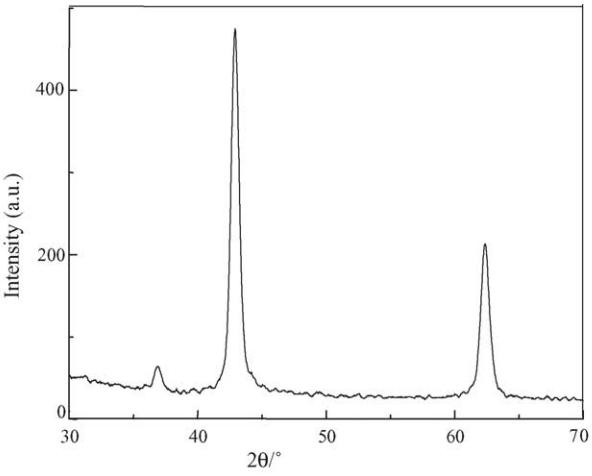
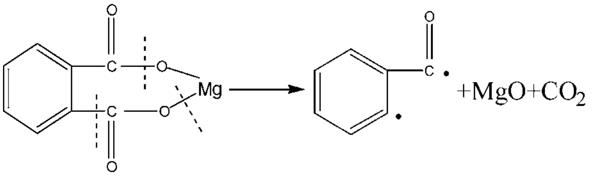
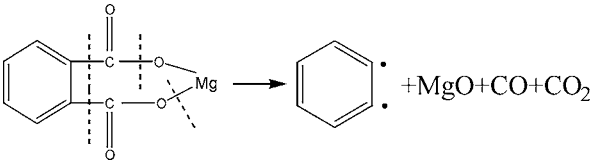


Fig. 3. The X-ray powder diffraction graph of solid product from decomposition of MgPht·$2H_2O$ at 750 °C in nitrogen.

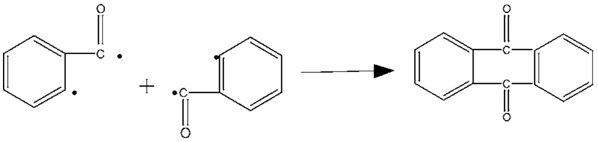


(1)



(2)

Two $^\bullet C_6H_4C(O)^\bullet$ were reacted to anthraquinone (see Eq. (3)):

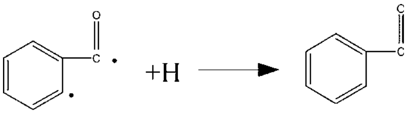


(3)

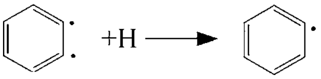
A part of $:C_6H_4$ was dehydrogenated easily to elemental C (Eq. (4)).

$$:C_6H_4 \rightarrow 6H + 4C \tag{4}$$

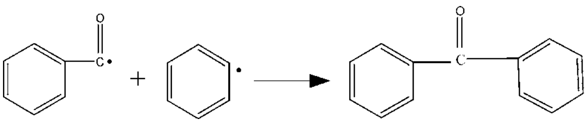
At the same time, the $^\bullet C_6H_4C(O)^\bullet$ and $:C_6H_4$ were hydrogenated according to Eqs. (5) and (6), to produce $C_6H_4C(O)^\bullet$ and $^\bullet C_6H_5$ and then benzophenone was obtained by Eq. (7):



(5)

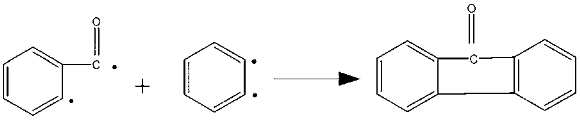


(6)



(7)

The presence of fluorenone in the products proved further the formations of free radicals described above.


(8)

Diphenylmethane, fluorine, triphenylmethane and 9-phenylfluorene were results of the reaction of benzophenone and fluorenone with H and $^{\bullet}C_6H_5$. The amount of these compounds is very small. This fact suggests that free radicals did not enter the gas phase, the reaction forming anthraquinone and benzophenone proceeded on the surface of solid products.

4. Conclusions

(1) Rheology phase reaction method is efficient, energy-saved, and economic for synthesizing. Magnesium phthalate can be obtained by the method, which is layered, monoclinic.
(2) Some important organic compounds such as anthraquinone, benzophenone can be obtained by thermal decomposition of magnesium phthalate, which are difficult to synthesis by conventional method. The thermal decomposition of magnesium phthalate offers a simpler way for preparing the kind of compounds.

Acknowledgements

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References

[1] R.N. Khlestkin, V.L. Khlestkina, Khim. Prom-st. (Moscow) 5 (1980) 271.
[2] P.S. Bassi, P.C. Kalsi, C.M. Khajuria, J. Therm. Anal. 18 (1980) 77.
[3] Cardarelli, G. D'Ascenzo, A.D. Magri, A. Pupella, Thermochim. Acta 33 (1979) 267.
[4] W. Brzyska, W. Wolodkiewica, J. Therm. Anal. 34 (1988) 1207.
[5] W. Brzyska, D. Wanczowska-Fonfara, J. Therm. Anal. 35 (1989) 727.
[6] W. Brzyska, W. Wolodkiewica, Thermochim. Acta 197 (1992) 1.
[7] W. Brzyska, P. Sadowski, Polish J. Chem. 58 (1984) 669.
[8] J.T. Sun, Z.H. Peng, X.Z. Du, Q.Y. Wang, Acta Chim. Binica 49 (1991) 1094.
[9] J.T. Sun, K.L. Zhang, J.M. Zhang, Z.B. Qin, Y.L. Fen, J. Chinese Univ. 11 (13) (1992) 1345.