Morphological control of zinc tricarbohydrazide perchlorate crystals: Theoretical and experimental study

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The theoretical crystal-morphology of zinc tricarbohydrazide perchlorate (ZnCP) was studied using the morphology simulation software. The growth trends and surface characteristics were calculated using the Bravais-Friedel-Donnay-Harker (BFDH), Growth Morphology, and Equilibrium Morphology methods; these provide theoretical guidance for the choice of crystal-control reagents. On the basis of the simulations, experiments were carried out to study the effects of five different crystal-control reagents, including carboxymethylcellulose (A), polyacrylamide (B), dextrin (C), Tween 40 (D), and Tween 60 (E), in the control of the crystal-morphology of ZnCP. Mixtures of two reagents and higher temperatures were used to further optimize the ZnCP crystals. The results show that ZnCP crystals are well dispersed, and have a large apparent density and regular crystal-morphology under the control of a mixture of reagents A and E in a mass ratio of 1:4 at 80°C.

physical chemistry, crystal-morphology, zinc tricarbohydrazide perchlorate (ZnCP), crystal-control reagent, morphology simulation

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The crystal-morphology of an energetic material has a direct effect on its physical properties such as fluidity, apparent density, electrostatic accumulation, and pressure resistance, and even has an important impact on its chemical and explosive properties such as stability, detonation ability, and sensitivity [1,2]. Generally, a material with a smooth surface, uniform particles, and spherical crystals has many advantages over needle- or twig-like irregular crystals, such as good fluidity, high apparent density (more than 0.8 g/cm³), low sensitivity, and stable performance [3,4]. A fine crystal-morphology plays an important role in the safety and stability of a material [5–7]. Methods for controlling crystal-morphology can therefore be used to regulate nucleation and crystal growth during the crystallization process to increase the production and use of security of energetic materials, and improve their energy output performances [8–12].

Zinc tricarbohydrazide perchlorate ([Zn(CHZ)₃](ClO₄)₂, ZnCP) is a new green energetic coordination compound that

excludes toxic heavy metals [13]. However, ZnCP crystals prepared using traditional synthetic techniques are too small, fragmented, and irregular, and have poor fluidity and a small apparent density (less than 0.7 g/cm³), leading to weak explosive power. Crystal-morphology control using a crystal-control reagent would improve the crystal quality, and enable ZnCP to be used as a green energetic material in practical applications.

In this study, the crystal-morphology and crystal-face parameters of ZnCP were simulated using the Morphology module of the Materials Studio simulation software (MS Morphology, Accelrys Corp., San Diego, CA, USA). Based on the theoretical calculations, experiments were performed to select the optimum crystal-control reagents and reaction conditions for the crystal-morphology optimization of ZnCP.

1 Theoretical study of crystal control

1.1 Morphology simulation

The Morphology module [14] can simulate crystal-mor-

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phology using crystal-structure data. It calculates the stable crystal-morphology under different conditions, giving specific crystal-face parameters such as the surface area, attachment energy, surface energy, and relative growth rate. It analyzes the effect of the relative growth rate on the crystal-morphology, providing a theoretical basis for the choice of crystal-control reagent [15,16].

The CIF file of the ZnCP crystal was imported into the MS Morphology software module and the crystal growth was simulated using three methods: the Bravais-Friedel-Donnay-Harker (BFDH), Growth Morphology, and Equilibrium Morphology methods. The theoretical crystal-morphologies are shown in Figure 1.

Simulation using the BFDH method shows that the crystal-morphology of ZnCP is a square block shape with a length/diameter ratio of 1.71. The crystal mainly consists of the (002), (10 $\bar{1}$), (101), and (011) faces and their symmetrical crystal-faces. The simulated morphology obtained using the Growth Morphology method is a long block shape with a length/diameter ratio of 1.97. It mainly consists of (002), (10 $\bar{1}$), (101), and (011) faces and their symmetrical crystal-faces. Among them, the (002), (10 $\bar{1}$), and (011) faces and their symmetrical crystal-faces occupy almost 90% of the total crystal-surface area. The morphology obtained using the Equilibrium Morphology method is an ellipsoid shape with a length/diameter ratio of 1.57. It consists of (002), (10 $\bar{1}$), (101), (011), (11 $\bar{1}$), and (10 $\bar{3}$) faces and their symmetrical faces. The main crystal-faces of ZnCP obtained using the three simulation methods are shown in Table 1. Taking these three models into consideration, the main crystal-faces, i.e. (002), (10 $\bar{1}$), (101), and (011), were determined, and their structures are presented in Figure 2.

The common features of the (002), (10 $\bar{1}$), (101), and (011) faces are the presence of an O atom (from ClO_4^-) and an N atom (from the CHZ ligand) in or near the crystal surface, and strong intermolecular interactions. Suitable crystal-control reagents should therefore have functional groups containing active H atoms. The H atoms of the crystal-control reagent can form hydrogen bonds with the O atoms of the crystal-face, and change the relative growth rate of the crystal-face, achieving the purpose of crystal-morphology

control.

1.2 Selection of crystal-morphology-control reagent

According to the Curie-Wulff principle [5], the vertical growth rate of the crystal-face is proportional to its surface tension. Surfactants, which are widely used as crystal-morphology-control reagents [17–20], can greatly reduce the surface tension, increase the diffusion coefficient of the solute and the viscosity of the reaction solution, and then reduce the rates of nucleation and crystal growth; these effects are conducive to primary explosive crystallization [21–25]. Based on the theoretical simulation results for ZnCP, the control reagents should have active H atoms in their functional groups. In addition, high efficiency, simple and easy procurement, low cost, and good compatibility with ZnCP should also be considered. Carboxymethylcellulose (A), polyacrylamide (B), dextrin (C), Tween 40 (D), and Tween 60 (E) were therefore selected as control reagents. A is an ionic surfactant and B, C, D, and E are non-ionic.

2 Experimental

2.1 Materials

$\text{Zn}(\text{ClO}_4)_2$ solution (1 mol/L) was prepared by the reaction of ZnO (powder, AR) and HClO_4 (solution). CHZ solution (2 mol/L) was obtained by dissolving solid CHZ (powder, AR) in deionized water. The crystal-morphology-control reagents A, B, C, D, and E (1 wt%) were prepared using these solutions. All the raw materials were commercial products and used without further purification.

2.2 Instruments

DCAT-21-type surface/interfacial tension test device (Data-physics Corp., Germany); the measurement range is 1–1000 mN/m with an accuracy of ± 0.001 mN/m. S-4800 cold-field-emission scanning electron microscope (SEM; Hitachi Corp., Japan); secondary electron detector, voltage 15 kV, resolution 1.0 nm, zoom magnification $\times 30$ to $\times 80000$.

Figure 1 (Color online) ZnCP crystal-morphology simulated using BFDH method (a), Growth Morphology method (b), and Equilibrium Morphology method (c).

Table 1 Proportions of main crystal-faces of ZnCP obtained using three simulation methods

Crystal face	BFDH (%)	Growth Morphology (%)	Equilibrium Morphology (%)
(002)	26.62	21.87	6.51
(10-1)	26.04	34.32	10.59
(101)	12.08	8.62	8.61
(011)	30.79	30.55	16
(11-1)	—	—	17.89
(10-3)	—	—	7.06
Total proportion	95.53	95.36	66.66

3 Results and discussion

3.1 Characterization of crystal-control reagent

The amount of crystal-control reagent for the optimum crystal-control effect is determined by the critical micelle concentration (CMC): the concentration of the crystal-control reagent should be slightly greater than the CMC. Solutions with different concentrations of crystal-control reagents were prepared at room temperature, and their surface tensions were measured. The curve of the dependence of the surface tension on concentration was plotted; the turning point of the curve represented the CMC. The results for

crystal-control reagent D are shown in Figure 3; the CMC is 0.00786 mass%. Using the same method, the CMC of C is 0.0623 mass%, and that of E is 0.0135 mass%. However, the viscosities of A and B are too large to accurately measure the surface tension, so the amounts of these are 0.1% to 0.3% of the total concentration.

3.2 Effects of single crystal-control reagent

The amount of the energetic material ZnCP synthesized was less than 10 g, to ensure safety. First, ZnCP crystals were prepared by a traditional synthetic method without any crystal-control reagents. $\text{Zn}(\text{ClO}_4)_2$ solution was added dropwise to CHZ solution at 60°C in 30±5 min, with a stirring speed of 250 r/min and a pH of 5 to 6. After keeping at a constant temperature for 10 min, ZnCP crystallized as the solution cooled down. The crystal-morphology without a control reagent is shown in Figure 4.

The crystals are irregular and have too many fragments. The crystal-morphology-control reagents were therefore added in different amounts in the synthetic process. All the morphologies were observed by SEM. The results are listed in Table 2. As an example, the crystal formed under the control of reagent E is shown in Figure 5.

The crystal-morphologies were improved by the crystal-control reagents. The shape is nearly regular and there are fewer fragments. Reagent A is an ionic surfactant, which

Figure 2 (Color online) Structures of crystal-faces of (002) (a), (10-1) (b), (101) (c), and (011) (d) for ZnCP.

Figure 3 Relationship between concentration and surface tension for reagent D.

Figure 4 Crystal-morphology of ZnCP without crystal-control reagent.

Table 2 Crystal-morphologies of ZnCP obtained using different reagents

Reagent	Amount (mL)	Yield (%)	Apparent density (g/cm ³)	Fluidity
A	0.5	89.4	0.74	Bad
	1	90.7	0.71	Bad
	2	88.5	0.69	Bad
B	2	88.1	0.79	Good
	4	87.2	0.75	Good
	6	84.6	0.67	Bad
C	2	69.0	0.71	Good
	4	80.1	0.73	Good
	8	88.6	0.67	Bad
D	1	83.0	0.75	Bad
	2	85.1	0.65	Bad
	4	88.0	0.74	Bad
E	1	86.4	0.70	Good
	2	87.5	0.73	Good
	4	91.8	0.72	Good

Figure 5 Crystal-morphology of ZnCP obtained using reagent E.

can form insoluble metal salts as nuclei for crystal growth. Reagents B, C, D, and E, as non-ionic surfactants, can greatly reduce the growth rate of the crystal-face to promote crystal growth, especially in the case of B, because of its high viscosity.

3.3 Synergistic effects of multiple crystal-control reagents and temperature

The effect of a single crystal-control reagent is very limited, and the obtained crystals have a non-uniform size and apparent density of less than 0.8 g/cm³; these ZnCP crystals do not meet the requirements for industrial applications. The synergistic effects of multiple crystal-control reagents were therefore explored. Because of the different advantages of ionic and non-ionic crystal-control reagents, A was combined with the B, C, D, and E, respectively, in different ratios. It was found that the synergistic effect of A and E in a mass ratio of 1:4 is most effective: the morphology is more regular and the crystals are larger. The ZnCP crystal-morphology obtained using A and E is illustrated in Figure 6. The compatibility of the crystal-control reagents and the reaction reagents should be considered, to avoid side effects. In this work, A, as an ionic surfactant, reacted with Zn(ClO₄)₂ to form an insoluble metal salts precipitate, and this should be avoided. Also, A and E cannot be mixed in large amounts, to avoid crystal bonding caused by high local concentrations of crystal-control reagents. Reagent A was therefore mixed with CHZ, forming the base solution, and E and Zn(ClO₄)₂ were the added solution. When Zn(ClO₄)₂ solution was added to the CHZ solution, the two crystal-control reagents play a synergistic role in controlling the ZnCP crystals.

Although the ZnCP crystals were further improved by the synergistic action of multiple crystal-control reagents, the apparent density was still lower than 0.8 g/cm³. The temperature is an important factor affecting the crystallization of primary explosives, so the reaction temperature was elevated from 60 to 70 and 80°C, with the other conditions remaining unchanged.

The results show that 80°C is the most suitable temperature.

Figure 6 Crystal-morphology of ZnCP obtained using reagents A and E (1:4).

Figure 7 Crystal-morphology of ZnCP obtained using A and E (1:4) at 80°C.

The crystal-control reagents A and E mixed in a mass ratio of 1:4 at 80°C therefore gave the best performance, as shown in Figure 7, with a yield of 92.3%, a neat morphology, good fluidity, and an apparent density of 0.86 g/cm³.

4 Conclusions

The crystal-morphology of ZnCP was predicted using the Morphology simulation software, which analyzed the characteristics of the main crystal-faces using three simulation methods. Analog calculations provided theoretical guidance for the choice of the crystal-morphology-control reagents. The effects of reagents A, B, C, D, and E and the temperature on control of the crystal-morphology were investigated experimentally by SEM examination of the crystals. The results reveal that the synergistic effect of complex reagents is much more apparent than that of a single reagent. In particular, a complex reagent consisting of ionic surfactant A and non-ionic surfactant E in a mass ratio of 1:4 at 80°C regulated the crystals, to give a neat and regular morphology, good fluidity, a high yield, and a large apparent density. Good-quality crystals guarantee the usage security and performance stability of ZnCP as a primary explosive in practical applications.

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