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Standard molar formation enthalpies of flower-like $NH_4CdPO_4 \cdot H_2O$

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Abstract Flower-like ammonium cadmium phosphate monohydrate was synthesized by solid-state reaction at low temperature and characterized by X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscope, and elemental analysis. The product $NH_4CdPO_4 \cdot H_2O$ was obtained with flower-like morphology by the addition of fatty alcohol-polyoxyethylene ether surface-active agent. Based on Hess's law, thermochemical cycle was designed to determine the dissolution enthalpies of reactants and products using a solution-reaction isoperibol calorimeter at 298.15 K, and the molar reaction enthalpy was calculated on the basis of above dissolution enthalpies. With the aid of other auxiliary thermodynamic data, the standard molar formation enthalpy of the title compounds was concluded: $\Delta_f H_m^{\ominus}[NH_4CdPO_4 \cdot H_2O] = (-1749.82 \pm 0.76)\ \mathrm{kJ\ mol^{-1}}$.

Keywords Ammonium cadmium phosphate monohydrate · Flower-like · Standard molar enthalpy of formation

Introduction

In the past two decades, new microporous materials have caused wide concern because of its structural diversity and potential application prospect in the field of adsorptive separation, ion exchange, catalyses, etc. Many phosphates such as $AlPO_4$-n, $NH_4MPO_4 \cdot H_2O$ ($M = Mn^{2+}$, Co^{2+}, Ni^{2+}, Fe^{2+}, Zn^{2+}, Cu^{2+}) are found to have micropore or mesopore structure and their catalytic property also has been verified by experiments [1]. Recently, more and more investigations have been made for their magnetic and intercalation properties [2, 3]. Considerable research interests are focused on new synthesis methods, shape, crystal plane effects, and molecular interaction of these compounds. Usually, metal phosphate with open-framework structure can be obtained by hydro-thermal or solvent-thermal method or solid-state reaction. Nieves et al. [4] prepared $NH_4FePO_4 \cdot H_2O$ using a mild hydrothermal technique, and the effect of addition of $NH_4FePO_4 \cdot H_2O$ on soil microbial activity was determined by calorimetry. Koleva [5, 6] investigated the metal–water (M^{2+}–H_2O), hydrogen bonding and the vibrational behavior of the phosphate ions in double phosphates $M'M''PO_4 \cdot H_2O$ ($M' = K^+$, NH_4^+; $M'' = Mn^{2+}$, Co^{2+}, Ni^{2+}) for the first time. Yin [7] prepared a novel ammonia cadmium phosphate with special morphology using template $N(C_2H_4)_3N$ at solid-state method at room temperature. Although there have been structural and spectroscopical reports on these compounds, to our knowledge, no reports about their morphology control and little or no thermodynamic data are available.

Properties of a compound are closely related to its particle morphology, which will affect on specific surface area, density, and chemical activity. In our previous papers [8], some metal phosphates, e.g., $NH_4MPO_4 \cdot H_2O$ ($M = Mn^{2+}$,

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Co^{2+}, Ni^{2+}, Fe^{2+}, Zn^{2+}, Cu^{2+}), have been prepared by solid-state reaction. Their standard molar enthalpies of formation have also been measured by calorimetry, a universal technique widely used for the measurements of enthalpies of reaction, dissolution and excess enthalpies in thermochemistry. These data of the standard molar formation enthalpy plays an important role in theoretical study, application development, and industrial production. The present work is a continuation of the previous investigation on the phosphates, which deals with the synthesis of petal-like $NH_4CdPO_4{\cdot}H_2O$ by solid-state reaction at low temperature and its standard molar enthalpy of formation by calorimetry at 298.15 K. These fundamental thermodynamical data will be important for further studies.

Experimental

Reagents

All the chemical reagents were analytical grade. KCl with purity higher than 99.99% was dried in a vacuum oven for 6 h at 393 K prior to use.

Preparation and characterization of $NH_4CdPO_4{\cdot}H_2O$

$(NH_4)_3PO_4{\cdot}3H_2O$ and $CdCl_2{\cdot}2.5H_2O$ were mixed with a molar ratio of 1:1. The mixture was ground for 60 min after the addition of fatty alcohol-polyoxyethylene ether (AEO-9) and then kept in an oven at 313.15 K for 48 h. The white crystals obtained were washed repeatedly with water until no Cl^- was detected in the filtrate. The crystals then were washed with ethanol and dried at 353.15 K. The products were identified by XRD (D/max-2500V diffractometer, Japan). The particle shape of SEM picture and EDS were determined by X-650 scanning Electronic Microscope (Japan) and GENESIS Energy Dispersive Spectrometer (EDAX Company, USA) and elemental analysis. Fourier transform infrared spectroscopy (FT-IR) was performed with MAGNA-IR550 equipment (Nicolet Company, USA). The FT-IR spectra were recorded from 400 to 4000 cm^{-1} using KBr pellets.

Calorimeter and calibration

The isoperibol reaction calorimeter, described in detail elsewhere [8, 9], was used for the investigation. The calorimeter was calibrated by the dissolution enthalpy of KCl (calorimetric primary standard) in water at 298.15 K. The measured average dissolution enthalpy was (17.47 ± 0.25) kJ mol^{-1} in agreement with the value of (17.54 ± 0.01) kJ mol^{-1} in the literature [10].

Calorimetric experiment

The selection of the calorimetric solvent is very important. It should dissolve the chemicals in the sample cell completely and rapidly, and it was found that the reactants and products could be dissolved completely in 4 mol L^{-1} HCl to give the same final state. To obtain the standard enthalpy of formation for $NH_4CdPO_4{\cdot}H_2O$, this compounds can be regarded as the product of reaction (1), and a thermochemical cycle designed as shown in Fig. 1. If the dissolution enthalpies of reactants $(\Delta_s H_1^\ominus, \Delta_s H_2^\ominus)$ and products $(\Delta_s H_3^\ominus, \Delta_s H_4^\ominus)$ were measured, the $\Delta_r H_m^\ominus$ and $\Delta_f H_m^\ominus$ of $NH_4CdPO_4{\cdot}H_2O$ can be obtained with the available auxiliary data. According to Hess's law, $\Delta_r H_m^\ominus = \Delta_s H_1^\ominus + \Delta_s H_2^\ominus - \Delta_s H_3^\ominus - 2\Delta_s H_4^\ominus - 4.5\Delta H_d^\ominus$.

$$CdCl_2 \cdot 2.5H_2O\ (s) + (NH_4)_3PO_4 \cdot 3H_2O\ (s) \rightarrow NH_4CdPO_4 \cdot H_2O\ (s) + 2NH_4Cl\ (s) + 4.5H_2O\ (l) \quad (1)$$

where $\Delta_s H_1^\ominus$, $\Delta_s H_2^\ominus$ is the dissolution enthalpies of two reactants in 4 mol L^{-1} HCl at 298.15 K, respectively; $\Delta_s H_3^\ominus$, $\Delta_s H_4^\ominus$ is the dissolution enthalpies of two of the products in 4 mol L^{-1} HCl at 298.15 K, respectively; $\Delta H_d^\ominus$ is the dilution enthalpy of water in 4 mol L^{-1} HCl at 298.15 K; $\Delta_r H_m^\ominus$ is the enthalpy value for the designed reaction.

Results and discussion

Identification of synthetic sample

XRD pattern of the product is showed in Fig. 2. Through comparison with the standard XRD of $NH_4CdPO_4{\cdot}H_2O$, it can be found that six stronger peaks (2θ data) of the product are at 10.060°, 31.040°, 25.540°, 38.630°, 20.361°, and 23.460°, respectively. The *d* values are 0.8786, 0.2879, 0.3485, 0.2329, 0.4358, and 0.3789, corresponding to the crystal plane indices of 010, 121, 131, 011, and 101. The patterns match the standard XRD data of $NH_4CdPO_4{\cdot}H_2O$ (JC PDF33-0048), and the XRD data are indexed as an orthorhombic system, with space group $Pmm2_1$: $a = 0.57289$ nm, $b = 0.88167$ nm, $c = 0.49098$ nm, and $V = 0.24799$ nm^3. The elemental analysis results of product are 5.70, 46.20, and 12.71% for nitrogen, cadmium, and phosphorous, respectively. The results are in good agreement with the calculated values 5.75, 46.18, and 12.72%, respectively. The energy dispersive spectrometer and its analysis results are showed in Fig. 3. From the mass fraction of cadmium, nitrogen, and phosphorus 5.22, 12.40, and 41.47% (not including carbon from conductive adhesive used in determination), the molar ratio of these

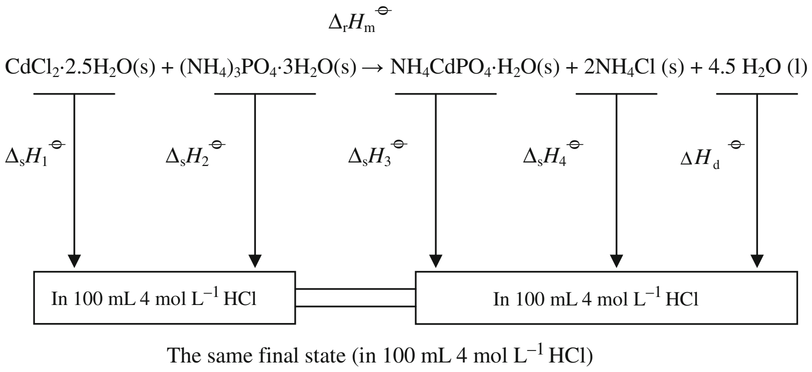


Fig. 1 Scheme of the thermochemical cycle of $NH_4CdPO_4·H_2O$

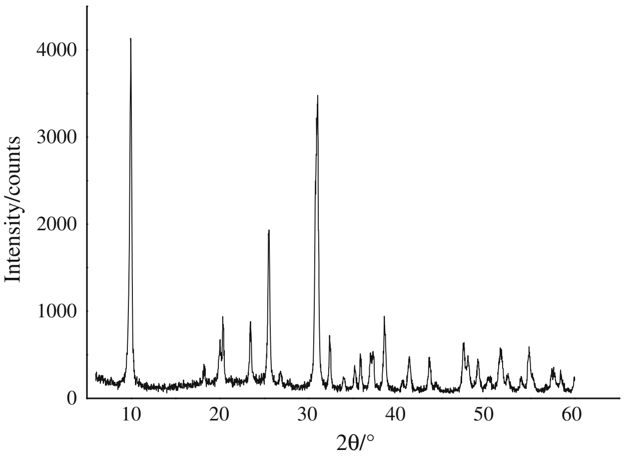


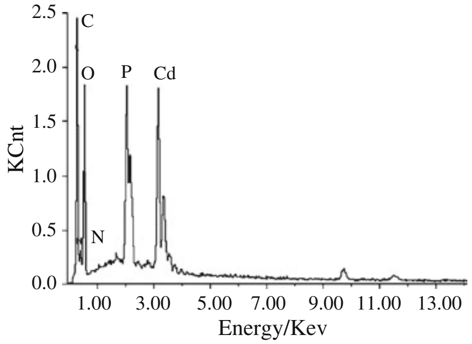
Fig. 2 XRD of $NH_4CdPO_4·H_2O$

elements can be calculated as Cd:N:P = 1:1:1, which is corresponding to molecular formula of $NH_4CdPO_4·H_2O$. All these results show the obtained products are pure $NH_4CdPO_4·H_2O$.

Previous studies found that addition of different surface-active agent can influence the particle shape and even particle size during the reaction. Reaction at low temperature instead of room temperature can improve crystallization. In solid-state reaction, non-ionic surfactants are usually used to control the particle morphology or size. In this work, AEO-9 is selected and applied to the stage of grinding in a mortar. SEM picture of the products is showed in Fig. 4. Obviously, addition of the surfactants caused the change of morphology of the products. Compared with the blocky granular shape obtained without surfactant AEO-9, flower-like particle is obtained by addition of AEO-9. Particle formation includes two stages: nucleation and growth. Influence of surfactant on surface energy of different crystal face is different. After nucleation, the reason of the flower-like morphology formation is that the particle grow along [010] crystal face under the role of surfactant AEO-9. The particle size of blocky granular product is >10 μm, but the petals of flower-like particle are submicron size (<0.1 μm). These results show the importance of non-surfactant AEO-9 in solid-state reaction at low temperature, which not only change the morphology but also decrease the particle size.

The FT-IR spectra (Fig. 5) of the two products are similar, which reflect characteristic stretching mode of NH_4^+, PO_4^{3-}. Water bonding at 1643 cm^{-1} and O–H stretching broad band centered at 3400–3300 cm^{-1} can be observed, implying the presence of crystalline hydrate. Absorption observed at 3265–2897 cm^{-1} and 1450 cm^{-1} were attributed to the N–H stretching mode of NH_4^+. The combining of both water stretching and N–H stretching result in the broad peak between 3400 and 2897 cm^{-1}. Absorption peak at 1081 cm^{-1} was attributed to the PO_4^{3-} asymmetric stretching mode and the sharp absorption peak at 970 cm^{-1} was attributed to the PO_4^{3-} symmetric stretching mode. The strong absorption bands at 500–700 cm^{-1} were attributed to PO_4^{3-} bending vibrations mode. Absorption

Fig. 3 EDS analysis results of $NH_4CdPO_4·H_2O$



Element	Wt %	At %
N K	05.22	09.96
O K	40.91	69.97
P K	12.40	10.10
CdL	41.47	09.97

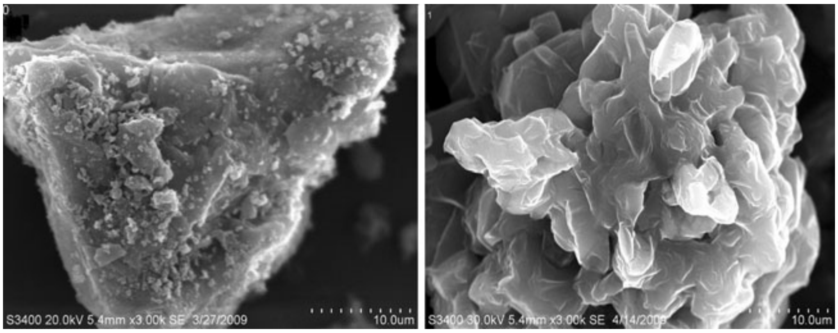


Fig. 4 SEM of $NH_4CdPO_4{\cdot}H_2O$ (*left*: non-AEO-9; *right*: adding AEO-9)

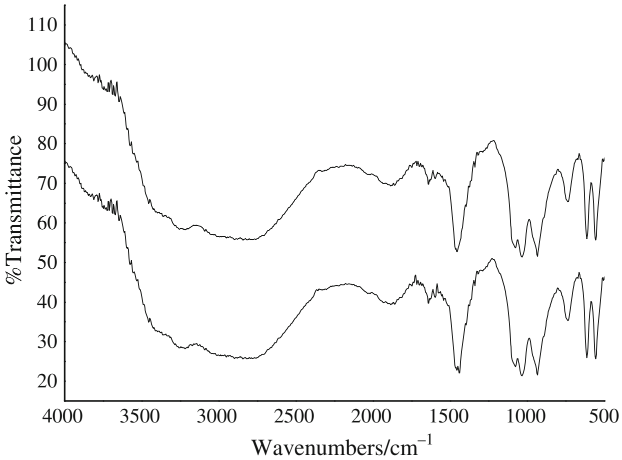


Fig. 5 FT-IR of the products (*up*: non-AEO-9)

Table 1 Dissolution enthalpies of $CdCl_2{\cdot}2.5H_2O$ (s) in 100 mL 4 mol L^{-1} HCl at 298.15 K

No	M ($CdCl_2{\cdot}2.5H_2O$)/g	Q/J	$\Delta_s H_1^{\ominus}$/kJ mol^{-1}
1	0.3430	40.228	26.783
2	0.3427	40.156	26.758
3	0.3430	40.395	26.894
4	0.3430	40.156	26.735
5	0.3428	39.787	26.505
6	0.3424	39.836	26.568
Ave			26.707 ± 0.141

Table 2 Dissolution enthalpies of $NH_4PO_4{\cdot}3H_2O$(s) in 100 mL 4 mol L^{-1} HCl at 298.15 K

No	M ($(NH_4)_3PO{\cdot}3H_2O$)/g	Q/J	$\Delta_s H_2^{\ominus}$/kJ mol^{-1}
1	0.3048	7.638	4.749
2	0.3048	7.670	4.769
3	0.3048	7.854	4.883
4	0.3048	7.634	4.746
5	0.3048	7.863	4.889
Ave		7.732 ± 0.101	4.807 ± 0.073

Table 3 Dissolution enthalpies of $NH_4CdPO_4{\cdot}H_2O$ (s) in 100 mL 4 mol L^{-1} HCl at 298.15 K

No	M ($NH_4CdPO_4{\cdot}H_2O$)/g	Q/J	$\Delta_s H_3^{\ominus}$/kJ mol^{-1}
1	0.1832	−11.817	−15.701
2	0.1833	−11.223	−14.904
3	0.1827	−11.302	−15.058
4	0.1825	−11.992	−15.993
5	0.1827	−11.336	−15.102
6	0.1831	−12.158	−16.1629
Ave			−15.487 ± 0.420

Table 4 Dissolution enthalpies of NH_4Cl (s) in 100 mL 4 mol L^{-1} HCl at 298.15 K

No	M (NH_4Cl)/g	Q/J	$\Delta_s H_4^{\ominus}$/kJ mol^{-1}
1	0.0803	27.191	18.116
2	0.0802	26.667	17.778
3	0.0802	26.887	17.925
4	0.0803	27.022	18.003
5	0.0802	26.781	17.854
6	0.0801	26.636	17.787
Ave			17.910 ± 0.132

Table 5 Ancillary data of standard enthalpies of formation at 298.15 K

Index	$\Delta_f H_m^{\ominus}$/kJ mol^{-1}	References
$(NH_4)_3PO_4{\cdot}3H_2O$, s	−2554.114 ± 0.141	[9]
NH_4Cl, s	−314.40	[12]
H_2O, l	−285.830 ± 0.042	[13]
$CdCl_2{\cdot}2.5\ H_2O$, s	−1131.94	[14]

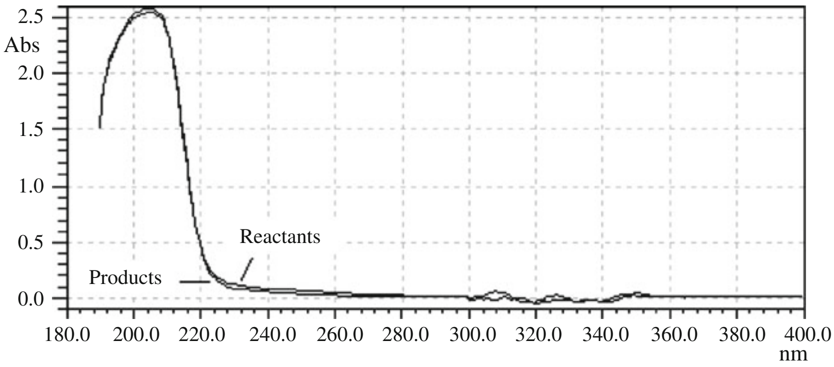


Fig. 6 Ultraviolet absorption spectrometry of reactions and products in 100 mL 4 mol L^{-1} HCl for thermochemical cycle of $NH_4CdPO_4 \cdot H_2O$

peak at near 1881 cm^{-1} was attributed to the free C=O stretching peak. Hence, AEO-9 used in the experiment is not a template but a dispersant during the grinding.

Determination of the molar dissolution enthalpies $\Delta_s H_1^\ominus$, $\Delta_s H_2^\ominus$, $\Delta_s H_3^\ominus$, and $\Delta_s H_4^\ominus$

Molar dissolution enthalpies of the reactants in 100 mL 4 mol L^{-1} HCl at 298.15 K were measured, as shown in Tables 1 and 2, respectively. The molar dissolution enthalpies of $NH_4CdPO_4 \cdot H_2O$ and NH_4Cl in 4 mol L^{-1} HCl at 298.15 K was shown in Tables 3 and 4, respectively.

Uncertainty $= \sqrt{\sum_{i=1}^{n} (x_i - \bar{x})^2/(n = 1)}$, in which n is the experiment times ($n = 5$), x_i is the experimental data of each measurement; $\bar{x}$ means average of results.

Calculation of ΔH_d

According to the literature [11], the dilution enthalpies of 4.5 mmol water in 100 mL 4 mol L^{-1} HCl at 298.15 K can be calculated as:

$$\begin{aligned}\Delta H_{d(4.000 \to 3.995)} &= \Delta H_{d(4.000 \to 0)} - \Delta H_{d(3.995 \to 0)} \\ &= -4433.45 - (-4428.90) \\ &= -0.00455 \text{ kJ mol}^{-1}\end{aligned}$$

Calculation of molar enthalpy of reaction and standard molar enthalpies of formation

Based on the obtained data, the molar enthalpy of reaction was calculated. From these values and various ancillary data in Table 5, the standard molar enthalpies of formation could also be calculated.

For $NH_4CdPO_4 \cdot H_2O$

$$\begin{aligned}\Delta_r H_m^\ominus &= \Delta_s H_1^\ominus + \Delta_s H_2^\ominus - \Delta_s H_3^\ominus - 2\Delta_s H_4^\ominus - 4.5\Delta H_d^\ominus \\ &= (11.201 \pm 0.741) \text{ kJ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta_f H_m^\ominus[NH_4CdPO_4 \cdot H_2O] = {} & \Delta_r H_m^\ominus \\ & + \Delta_f H_m^\ominus[CdCl_2 \cdot 7.5H_2O] \\ & + \Delta_f H_m^\ominus\left[(NH_4)_3PO_4 \cdot 3H_2O\right]\end{aligned}$$

$$\begin{aligned}& -2\,\Delta_f H_m^\ominus[NH_4Cl] - 4.5\Delta_f H_m^\ominus[H_2O] \\ & = (-1749.82 \pm 0.76) \text{ kJ mol}^{-1}\end{aligned}$$

Determination of the final state of the reaction

The UV–Vis spectra (see Fig. 6) of the final solution of the reactants and the products could also be used to determine whether they have the same thermodynamic state. The ultraviolet absorption of solution obtained by dissolving reactant or the product in 100 mL 4 mol L^{-1} HCl completely overlaps each other with the maximum absorption wavelength. Conductivity values after 500 times diluted are 1989 and 1991 μs cm^{-1}, respectively. Refractive indexes are 1.3228 and 1.3227, respectively. All these results show both reactant and the product have the same dissolved state to ensure realization of the thermochemistry cycle. Therefore, we believed these standard enthalpies determined by solution-reaction calorimetry were reliable.

Conclusions

Solid-state reaction at low temperature can be used to prepare $NH_4CdPO_4 \cdot H_2O$. Non-ionic surfactants AEO-9 can influence the particle shape. Compared with the blocky granular shape obtained without surfactant addition, flower-like particle can be obtained by addition of non-ionic surfactants AEO-9. The standard molar formation enthalpy of the flower-like $NH_4CdPO_4 \cdot H_2O$ is: $\Delta_f H_m^\ominus(NH_4CdPO_4 \cdot H_2O) = (-1749.82 \pm 0.76) \text{ kJ mol}^{-1}$.

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