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Standard molar enthalpies of formation for a series of microporous crystals of $Na_2[M^{II}B_3P_2O_{11}(OH)]\cdot 0.67H_2O$ (M^{II} = Mg, Mn, Fe, Co, Ni, Cu, Zn)

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ABSTRACT

The microporous crystal of $Na_2[CoB_3P_2O_{11}(OH)]\cdot 0.67H_2O$ has been synthesized under hydrothermal conditions and characterized by XRD, FT-IR, DTA-TG techniques and chemical analysis. The molar enthalpies of solution of $Na_2[CoB_3P_2O_{11}(OH)]\cdot 0.67H_2O$ (s) in 1 mol·dm^{-3} HCl (aq), of $NaH_2PO_4\cdot 2H_2O$ (s) in (H_3BO_3 + HCl + H_2O) (aq), and of $CoCl_2\cdot 6H_2O$ (s) in ($NaH_2PO_4\cdot 2H_2O$ + H_3BO_3+HCl + H_2O) (aq) were measured, respectively. With the incorporation of the previously determined enthalpy of solution of H_3BO_3 (s) in 1 mol·dm^{-3} HCl (aq), together with the use of the standard molar enthalpies of formation for $CoCl_2\cdot 6H_2O$ (s), $NaH_2PO_4\cdot 2H_2O$ (s), H_3BO_3 (s), HCl (aq) and H_2O (l), the standard molar enthalpy of formation of – (5104.7 ± 2.6) kJ·mol^{-1} for $Na_2[CoB_3P_2O_{11}(OH)]\cdot 0.67H_2O$ at T = 298.15 K was obtained on the basis of the appropriate thermochemical cycle. In addition, the molar enthalpy of formation of −4373.9 kJ·mol^{-1} for $[B_3P_2O_{11}(OH)]^{4-}$ has also estimated by a group contribution method, which has been used to predict the $\Delta_f H^\circ_m$ of the others four kinds of $Na_2[M^{II}B_3P_2O_{11}(OH)]\cdot 0.67H_2O$. These estimated data have been further used to compare the stabilities of this series of compounds.

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1. Introduction

Borophosphates have attracted considerable interest since the last decade for their potential applications as redox catalysts, molecular sieves and ion exchangers [1,2]. Until now, many borophosphates have been synthesized, some of which possessed 3D open framework structures and might be used as microporous materials, such as a series of microporous crystals of $Na_2[M^{II}B_3P_2O_{11}(OH)]\cdot 0.67H_2O$ (M^{II} = Mg, Mn, Fe, Co, Ni, Cu, Zn) [3].

Thermodynamic properties play very important roles in scientific research and industrial applications. Thermochemical data can provide information on stabilities and reactivities of molecules that are used, and also are a key factor in the safe and successful scale-up of chemical processes in the chemical industry. Navrotsky group has done much work on the thermochemistry of microporous compounds such as zeolites, pure silica, gallosilicate, and aluminophosphates by using high-temperature calorimetry [4,5]. Our group has also reported the determination of standard molar enthalpies of formation of two borophosphates with microporous structure, $Na_2[CuB_3P_2O_{11}(OH)]\cdot 0.67H_2O$ and $Na_2[ZnB_3P_2O_{11}(OH)]\cdot 0.67H_2O$, by using a heat conduction microcalorimeter [6,7].

As part of the continuing study of this work, this paper reports the determination of standard molar enthalpy of formation of $Na_2[CoB_3P_2O_{11}(OH)]\cdot 0.67H_2O$ by solution calorimetry, and the estimation of the standard molar enthalpies of formation for this series of microporous crystals of $Na_2[M^{II}B_3P_2O_{11}(OH)]\cdot 0.67H_2O$ (M^{II} = Mg, Mn, Fe, Co, Ni, Cu, Zn) by a group contribution method on the basis of those measured results.

2. Experimental

2.1. Synthesis and characterization of sample

$Na_2[CoB_3P_2O_{11}(OH)]\cdot 0.67H_2O$ was synthesized referring to literature [3], and all reagents used in the synthesis were of analytic grade. 1.41 g of $CoSO_4\cdot 7H_2O$, 7.63 g of $Na_2B_4O_7\cdot 10H_2O$ and 3 cm^3 of concentrated H_3PO_4 (14.6 mol·dm^{-3}) were charged into a Teflon-lined stainless steel vessel, and heated at T = 473 K for 4 days. After cooling to room temperature, the solid product was washed with hot water (T = 353 K) until the soluble component was completely removed, and finally dried at room temperature to constant mass. The sample was characterized by X-ray powder diffraction (Rigaku D/MAX-IIIC with Cu target at 8°·min^{-1}), FT-IR spectroscopy (recorded over the 400 to 4000 cm^{-1} region on a Nicolet NEXUS 670 FT-IR spectrometer with KBr pellet at room temperature), and TG-DTA (performed on a TA-SDT Q600 simultaneous thermal analyzer under N_2 atmosphere with a heating rate of 10 K·min^{-1}).

The chemical compositions of the sample were determined by EDTA titration for Co^{2+}, by NaOH standard solution in the presence of mannitol for B_2O_3, and by the mass loss in the TG curve for H_2O.

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2.2. Calorimetric experiment

The 1 mol·dm^{-3} HCl (aq) solvent can dissolve all components of the reaction (6) in the designed thermochemical cycle as shown in figure 1, and its concentration of 1.0004 mol·dm^{-3} was determined by titration with standard sodium carbonate. With the use of its density of 1.019 g·cm^{-3} (taken from chemical handbook [8]), its concentration can also be expressed as the form of HCl·54.561H_2O. The molar enthalpies of solution of $Na_2[CoB_3P_2O_{11}(OH)]\cdot 0.67H_2O$ (s), H_3BO_3 (s), $NaH_2PO_4\cdot 2H_2O$ (s), and $CoCl_2\cdot 6H_2O$ (s) in corresponding solvents were measured, respectively. In all these determinations, strict control of the stoichiometries in each step of the calorimetric cycle must be observed, with the objective that the dissolution of the reactants give the same composition as those of the products.

Applying Hess's law, $\Delta_r H^o_m$ (6) can be calculated according to the following expression:

$$\Delta_r H^o_m(6) = \Delta_r H^o_m(1) - \Delta_r H^o_m(2) - \Delta_r H^o_m(3) - \Delta_r H^o_m(4) - \Delta_r H^o_m \quad (5)$$

The standard molar enthalpy of formation of $Na_2[CoB_3P_2O_{11}(OH)]\cdot 0.67H_2O$ can be obtained by the values of $\Delta_r H^o_m$ (6) in combination with the standard molar enthalpies of formation of $CoCl_2\cdot 6H_2O$ (s), $NaH_2PO_4\cdot 2H_2O$ (s), H_3BO_3 (s), HCl (aq) and H_2O (l).

All the enthalpies of solution were measured with a RD496-2000 heat conduction microcalorimeter (Mianyang CP Thermal Analysis Instrument Co., LTD, China), which has been described in detail previously [9]. The total time required for the complete dissolution reaction was about 0.5 h. There were no solid residues observed after the reactions in each calorimetric experiment.

To check the performance of the calorimeter, the enthalpy of solution of KCl (mass fraction $\geqslant$0.9999) in deionized water was determined to be (17.54 ± 0.10) kJ·mol^{-1}, which was in agreement with that of (17.524 ± 0.028) kJ·mol^{-1} reported in the literature [10]. This shows that the device used for measuring the enthalpy of solution in this work is reliable.

3. Results and discussion

3.1. Characterization of synthetic sample

Figure 2 shows the powder XRD pattern of as-synthesized compound and the simulated pattern on the basis of single-crystal structure of $Na_2[CoB_3P_2O_{11}(OH)]\cdot 0.67H_2O$. The diffraction peaks on patterns corresponded well in position, indicating the phase purity of the as-synthesized sample.

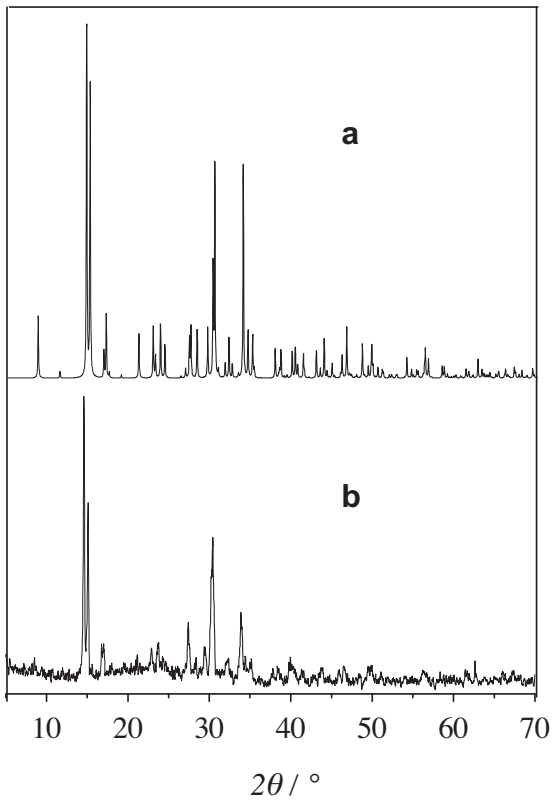

FIGURE 2. X-ray powder diffraction pattern of synthetic sample: (a) simulated and (b) experimental.

The FT-IR spectrum of synthetic sample (figure 3) exhibited the following absorption bands and they were assigned referring to the literature [3,11]. The band at 3433 cm^{-1} is the stretching vibration of the O-H group. The band at 1628 cm^{-1} is assigned to the H-O-H bending mode, which shows this compound contains crystal water. The bands between (600 and 1500) cm^{-1} might belong to the B-O and P-O asymmetric stretch in [BO_3], [BO_4] and [PO_4] groups. These assignments are consistent with its structure of $Na_2[CoB_3P_2O_{11}(OH)]\cdot 0.67H_2O$ [3].

The simultaneous TG–DTA curves of synthetic sample (figure 4) indicate that the total mass loss is 5.67% over the temperature range of (400 to 850) K, which corresponds to the loss of 1.17 water molecules and agrees with the calculated value of 5.21%. In the

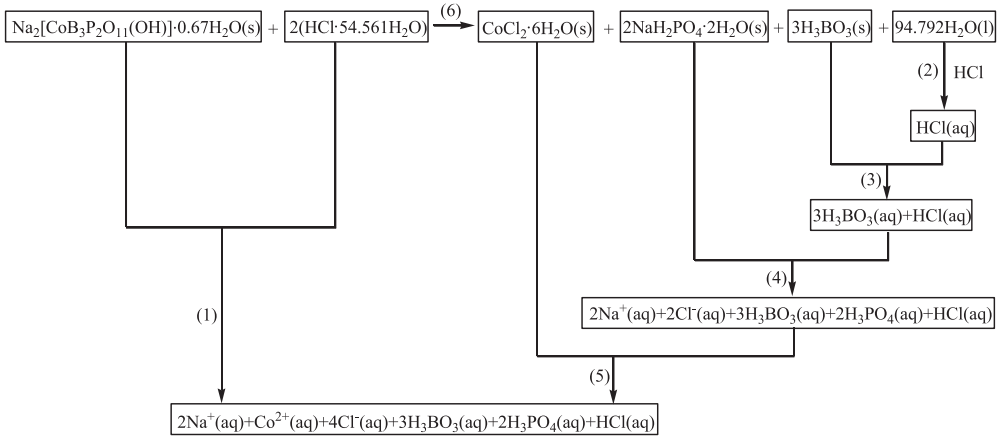

FIGURE 1. Schematic drawing of the thermodynamic circle.

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