J. Chem. Thermodynamics 101 (2016) 157–161

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

Thermodynamic properties of two microporous materials for $Na_2[M_2B_{12}O_{21}]$ (M = Co^{2+}, Cu^{2+})

Yong-Jie Geng, Jie Wang, Zhi-Hong Liu *

Key Laboratory for Macromolecular Science of Shaanxi Province, School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an 710062, PR China

ARTICLE INFO

Article history:
Received 8 May 2016
Received in revised form 26 May 2016
Accepted 30 May 2016
Available online 30 May 2016

Keywords:
Transition metal borate
Microporous materials
Standard molar enthalpy of formation
Solution calorimetry

ABSTRACT

Two transition metal borates with microporous structures for $Na_2Co_2B_{12}O_{21}$ and $Na_2Cu_2B_{12}O_{21}$ have been synthesized and characterized by XRD, FT-IR, and elemental analysis. The molar enthalpies of solution of $Na_2Co_2B_{12}O_{21}$(s) and $Na_2Cu_2B_{12}O_{21}$(s) in 1 mol dm^{-3} HCl(aq) were measured by microcalorimeter at T = 298.15 K, respectively. The molar enthalpies of solution of $CoCl_2{\cdot}6H_2O$(s) and $CuCl_2{\cdot}2H_2O$(s) in the mixture solvent of 2.00 cm^3 of 1 mol dm^{-3} HCl(aq) in which 5.30 mg of H_3BO_3 and 0.84 mg of NaCl being added were also 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 standard molar enthalpies of formation for $CoCl_2{\cdot}6H_2O$(s)/$CuCl_2{\cdot}2H_2O$(s), NaCl(s), H_3BO_3(s), HCl(aq) and H_2O(l), the standard molar enthalpies of formation of – (9072.4 ± 9.7) kJ mol^{-1} for $Na_2Co_2B_{12}O_{21}$(s) and – (8887.5 ± 9.7) kJ mol^{-1} for $Na_2Cu_2B_{12}O_{21}$(s) at T = 298.15 K were obtained on the basis of the appropriate thermochemical cycles. It is obvious that $Na_2Co_2B_{12}O_{21}$(s) is more thermal stable than that of $Na_2Cu_2B_{12}O_{21}$(s).

1. Introduction

Microporous materials have attracted considerable attention due to their widespread applications in catalysis, ion exchange, and adsorption [1]. Boron can form a large variety of compounds because of the complexity of the structures involved. Until now, the boron atom has been introduced in several frameworks of microporous material systems, such as B-O-M (transition metal) system. Many transition metal borates have been synthesized, some of which possessed three-dimensional open framework structures and might be used as microporous materials, such as two transition metal borates with microporous structures, $Na_2Co_2B_{12}O_{21}$ [2] and $Na_2Cu_2B_{12}O_{21}$ [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 reported the thermodynamic properties of several boron-containing microporous materials [6–10]. As part of the continuing study of this work, this paper reports the determination of standard molar enthalpies of formation of two transition metal borates microporous materials of $Na_2Co_2B_{12}O_{21}$ and $Na_2Cu_2B_{12}O_{21}$ by using a heat conduction microcalorimeter.

2. Experimental

2.1. Synthesis and characterization of samples

The microporous crystal samples were synthesized referring to literature [2,3] by using high temperature solid-state reactions. All reagents used in the synthesis were of analytic grade. Table 1 summarizes relevant information on sample material purities.

The powder products obtained were washed with hot distilled water, and dried in air at ambient temperature. The sample was characterized by X-ray powder diffraction (Rigaku D/MAX-IIIC X-ray diffractometer with Cu target at 8°·min^{-1}), and FT-IR spectroscopy (recorded over the 400–4000 cm^{-1} region on a Nicolet NEXUS 670 FT-IR spectrometer with KBr pellet at room temperature). The content of B_2O_3 in the sample was determined by NaOH standard solution in the presence of mannitol. The content of Na^+ in the sample was determined by ICP-MS (performed on a Bruker M90).

* Corresponding author.
E-mail address: liuzh@snnu.edu.cn (Z.-H. Liu).

http://dx.doi.org/10.1016/j.jct.2016.05.026
0021-9614/

Table 1
Provenance and mass fraction purity of the chemical reagents used in this study.

Chemical name	Source	State	Mass fraction purity [a]
$CoCl_2{\cdot}6H_2O$	Sinopharm Chemical Reagent Co., Ltd.	Solid	⩾0.993
$CuCl_2{\cdot}2H_2O$	Peking Chemical Works	Solid	⩾0.990
H_3BO_3	Xian Chemical Reagent Factory	Solid	⩾0.990
$Na_2B_4O_7{\cdot}4H_2O$	Sinopharm Chemical Reagent Co., Ltd.	Solid	⩾0.995
$Co(CH_3COO)_2{\cdot}4H_2O$	Sinopharm Chemical Reagent Co., Ltd.	Solid	⩾0.995
$Cu(CH_3COO)_2{\cdot}H_2O$	Sinopharm Chemical Reagent Co., Ltd.	Solid	⩾0.990
$Ni(CH_3COO)_2{\cdot}4H_2O$	Aladdin	Solid	⩾0.980
KCl	Aladdin	Solid	⩾0.9999
HCl	Sinopharm Chemical Reagent Co., Ltd	aqueous	0.38 [b]
$Na_2Co_2B_{12}O_{21}$	Synthesized	Solid	0.994 [c]
$Na_2Cu_2B_{12}O_{21}$	Synthesized	Solid	0.993 [c]

[a] Stated purity from the commercial supplier.
[b] Concentration of HCl aqueous solution.
[c] Evaluated by averaging based on the measured contents of B_2O_3 and Na^+.

2.2. Calorimetric experiments

$Na_2Co_2B_{12}O_{21}$ and $Na_2Cu_2B_{12}O_{21}$ can be regarded as the product of the reaction (6) in the designed thermochemical cycles as depicted in Figs. 1 and 2, respectively.

The 1 mol dm^{-3} HCl(aq) solvent can dissolve all components of the reaction (6), 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 [11]), its concentration can also be expressed as the form of $HCl{\cdot}54.561H_2O$.

The molar enthalpies of solution of 4.49 mg of $Na_2Co_2B_{12}O_{21}$ and 4.56 mg of $Na_2Cu_2B_{12}O_{21}$ in 1 mol·dm^{-3} HCl(aq) were measured, respectively. The molar enthalpies of solution of 3.40 mg of $CoCl_2{\cdot}6H_2O$(s) and 2.43 mg of $CuCl_2{\cdot}2H_2O$(s) in the mixture solvent of {2.00 cm^3 of 1 mol dm^{-3} HCl + 5.30 mg of H_3BO_3 + 0.84 mg of NaCl (aq)} were also 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, $\Delta_r H^\theta_m$ (6) can be calculated according to the following expression:

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

The standard molar enthalpies of formation of $Na_2Co_2B_{12}O_{21}$ and $Na_2Cu_2B_{12}O_{21}$ can be obtained by the values of $\Delta_r H^\theta_m$ (6) in combination with the standard molar enthalpies of formation of NaCl(s), $CoCl_2{\cdot}6H_2O$(s)/$CuCl_2{\cdot}2H_2O$(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 [12,13]. Calorimetric experiments were performed five times at T = 298.15 K. 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(s) (mass fraction ⩾ 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 [14]. 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 samples

Figs. 3 and 4 show the powder XRD patterns of as-synthesized samples and the simulated patterns on the basis of single-crystal structures of $Na_2Co_2B_{12}O_{21}$ and $Na_2Cu_2B_{12}O_{21}$, respectively. The diffraction peaks on patterns for $Na_2Co_2B_{12}O_{21}$ and $Na_2Cu_2B_{12}O_{21}$ samples corresponded well in position respectively, indicating the phase purity of the as-synthesized samples.

As shown in Fig. 5, the FT-IR spectra of these two synthesized samples are also very similar, which indicate their similar structures. The FT-IR spectrum of $Na_2Co_2B_{12}O_{21}$ sample exhibits the following absorption bands, which are assigned referring to

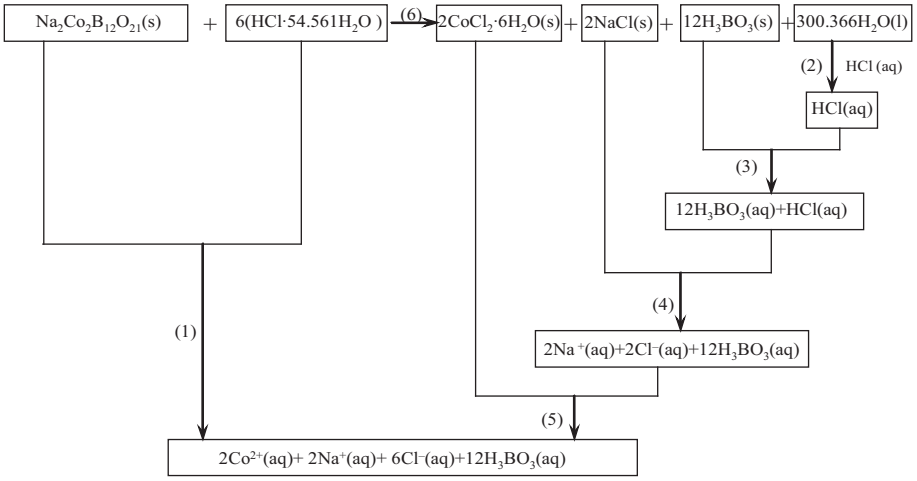

Fig. 1. Schematic drawing of the thermochemical circle for $Na_2Co_2B_{12}O_{21}$(s).