

The Effect of The Reaction Conditions on The Synthesis and Characterization of Potassium Borate from Potassium Chloride

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Abstract

In this study, the synthesis and characterization of potassium borate were studied using KCl, NaOH and H₃BO₃ as the starting materials. The effects of the boron precursor, reaction temperature and time on the structure of the synthesized potassium borate were investigated. X-ray diffraction (XRD) showed the synthesized sample was santite, which has the chemical formula KB₅O₈·4H₂O (Powder diffraction file number: 01-1072-1688). The XRD scores increased upon decreasing the reaction temperature and time. The characteristic band values observed for boron and oxygen were investigated using Fourier transform infrared (FT-IR) and Raman spectroscopy. The morphology of the synthesized samples was characterized using scanning electron microscopy (SEM). The samples were found to be on the micro-scale with particle sizes <2.54 μm. The reaction yields were in the range of 75.01–95.03% for Set-1 and 72.04–92.22% for Set-2.

Keywords: Hydrothermal synthesis, potassium borate, spectroscopy, SEM, XRD

1. INTRODUCTION

Borate is the general name used to describe boron containing compounds. In general, metals bond with triangularly coordinated boron atoms (B₍₃₎-O) or tetrahedrally coordinated boron atoms (B₍₄₎-O). Metal borates can also be categorized according to the metal atom in their structure, for example, sodium borates, calcium borates, magnesium borates, zinc borates and potassium borates. Metal borates have notable physical and chemical properties, and therefore, they are widely used in a range of industrial applications. Each type of metal borate has unique features that are preferred in different areas of application [1, 2]. Potassium borates are a specific type of boron compound, which have been used in the preparation of non-linear optical materials, antibiotics and high temperature fluxes [3, 4].

There are several types of potassium borate compounds prepared in the K₂O–B₂O₃–H₂O system including KB₃O₄(OH)₂, K₂B₅O₈(OH)·2H₂O, K[B₅O₇(OH)₂], K₄B₁₀O₁₅(OH)₄, K₂B₅O₈·4H₂O, KBO₂ and KBH₄. The general synthesis procedure used to prepare potassium borate involves hydrothermal conditions at a constant reaction temperature and time. For example, KB₃O₄(OH)₂ has been prepared using a hydrothermal method under autogenous pressure in a mixture of dimethylformamide-water at the crystallization temperature of 165 °C over 10 days [5]. K₂B₅O₈(OH)·2H₂O is synthesized upon heating K₂CO₃ and H₃BO₃ in an aqueous medium at 170 °C for 7 days [6]. K[B₅O₇(OH)₂] has been produced as colorless crystals from

GaO(OH), KNO₃ and H₃BO₃ upon heating at 210 °C for 3 days [7]. K₄B₁₀O₁₅(OH)₄ is obtained by heating KOH, H₃BO₃ and pyridine in an aqueous medium at 170 °C over 7 days [8]. Svanson et al. obtained potassium borate glass at the melting point of a mixture comprised of K₂CO₃ and H₃BO₃ [9]. Alicilar et al. have determined the fire retardant properties of KBO₂ [10], Dovgaliuk et al. have studied the hydrolysis of KBH₄ in the presence of CO₂ [11], and Youngman and Zwanziger have studied the NMR and Raman spectra of potassium borate glass [12].

It is apparent from the literature the conventional approach used to prepare potassium borate involves the dissolution of the starting materials, the addition of a catalyst (if any) and heating the reaction mixture at a temperature higher than the boiling point of the liquid medium over a prolonged period of time (usually >3 days). Therefore, the synthesis of potassium borate may require the use of complicated apparatus, such as a leakproof and pressure resistant steel reactor. The aims of the present study was to investigate the effects of the reaction conditions on the synthesis of potassium borate hydrate and its characterization with the objective to simplify the synthetic procedure for industrial applications. The results showed moderate reaction conditions (reaction temperature: 60–90 °C and reaction time: 15–120 min) can be used to prepare potassium borate. The synthesized samples were identified using X-ray diffraction (XRD) and characterised using Fourier transform infrared (FT-IR) and Raman spectroscopy. The

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morphological properties were investigated using scanning electron microscopy (SEM).

2. MATERIAL AND METHODS

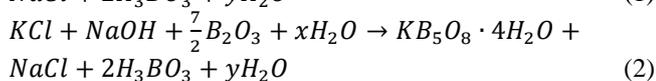
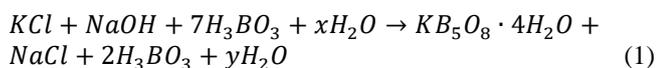
2.1. Starting Material Preparation and Characterization

The starting materials used in the experiments were potassium chloride (KCl), boric acid (H_3BO_3), boron oxide (B_2O_3) and sodium hydroxide (NaOH). KCl was used as the potassium source and obtained from Sigma-Aldrich (CAS Number P9333 with a minimum purity of 99%), which was used without any further purification. NaOH was used as the sodium ion source to capture the Cl^- ions generated during the reaction. Boric acid (H_3BO_3) and boron oxide (B_2O_3) were used as the boron precursors, which were processed prior to use via crushing, grinding and sieving to reduce the particle size to $<75 \mu m$.

The starting materials were identified by XRD on a PANalytical XPert Pro X-ray diffractometer (PANalytical, Almelo, The Netherlands) using $Cu-K\alpha$ radiation. The operating parameters of the device were in the 2θ range of $7-90^\circ$, 45 kV and 40 mA ($\lambda = 1.53 \text{ nm}$).

2.2. Hydrothermal Synthesis of Potassium Borate

In the hydrothermal synthesis of potassium borate, two different sets were prepared using H_3BO_3 and B_2O_3 as the boron precursors. In both sets, KCl was used as the potassium source. In Set-1, KCl and NaOH were reacted with H_3BO_3 , whereas in Set-2, KCl and NaOH were reacted with B_2O_3 . The reaction sets can be described with the codes Kc-Na-H and Kc-Na-B for Set-1 and Set-2, respectively. Each product was encoded by the letters, Kc: KCl, Na: NaOH, H: H_3BO_3 and B: B_2O_3 , the reaction temperature and reaction time. For instance, the sample synthesized at $90^\circ C$ for 30 min in Set-1 was coded as "Kc-Na-H-90-30". The molar ratio of potassium to boron precursor used in the reactions was 1:7 and the reactions were performed in a 50 mL glass reaction vessel. In Set-1, 0.129 mmol of H_3BO_3 was dissolved in pure water (25 mL) and 0.0184 mmol of KCl and 0.020 mmol of NaOH were added to the resulting solution. In Set-2, the same quantities of KCl and NaOH as Set-1 were added to a solution of 0.065 mmol of B_2O_3 dissolved in pure water (25mL). The reactions were performed under magnetic stirring at 500 rpm and the reaction temperature and time were varied in the range of $60-90^\circ C$ and 15–120 min, respectively. The expected reactions are given in equations (1) and (2).



The reaction yields were calculated using the procedure of Derun et al. [13]. KCl was selected as the key component in

the calculation of the reaction yield. The overall yield (Y_D) was calculated by dividing the number of moles of the final product (N_D) by the number of moles of the key reactant (A) consumed during the reaction. The value for A was calculated using the initial (N_{A0}) and final (N_A) number moles of reactant in the reaction. For the batch system, the equation can be rewritten as equation (3) [13].

$$Y_D = \frac{N_D}{N_{A0} - N_A} \quad (3)$$

The calculations used to determine the reaction yield were carried out in triplicate.

2.3. Characterization of The Synthesized Potassium Borate Products

The synthesized potassium borate products were identified using XRD. The XRD parameters are described in Section 2.1. The characteristic band values of the samples were analyzed using a Perkin Elmer FT-IR spectrometer equipped with a universal attenuation total reflectance (ATR) sampling accessory and diamond/ZnSe crystal. The FT-IR spectra were recorded in the range of $1500-650 \text{ cm}^{-1}$ using 4 scans at a resolution of 4 cm^{-1} . For further analysis, the Raman spectra of the samples were recorded on a Perkin Elmer Brand Raman Station 400 F spectrometer in the range of $1200-250 \text{ cm}^{-1}$ at intervals of 2 cm^{-1} with an exposure time of 4 seconds over 4 exposures. A CamScan Apollo 300 field-emission scanning electron microscope (15 kV, magnification: 2000) was used to study the surface morphology of the as-prepared samples.

3. RESULTS AND DISCUSSION

3.1. Characterization of the starting materials

Potassium chloride was used as the potassium source and identified as Sylvite KCl (Powder diffraction file number: 00-041-1476). The boron precursors used in the experiments were identified as boric acid (H_3BO_3) and boron oxide (B_2O_3) in accordance with the powder diffraction file numbers 01-073-2158 and 00-006-0297, respectively.

3.2. The XRD Results Obtained for The Synthesized Potassium Borate Products

Based on the XRD results, the synthesized potassium borate structure was identified as the santite with the chemical formula $KB_5O_8 \cdot 4H_2O$ (powder diffraction file number 01-1072-1688). The optimum samples were identified according to their XRD scores, which represent the consistency of the observed peak intensities (%) and peak locations with the reference card. The XRD results of the synthesized potassium borate samples are given in Table 1. Higher XRD scores were observed in the products formed at lower temperature and time in both sets, which may be attributed to the stability of the potassium borate hydrate structure at higher temperature.

In Set-1 (Kc-Na-H), higher XRD scores were seen at a reaction temperature of $60^\circ C$. The reaction time has only a minor effect on the formation of the santite product at $60^\circ C$

as confirmed by the minor differences observed between the as-obtained products. The XRD scores of the synthesized potassium borate samples decreased upon increasing the reaction temperature and time. The highest XRD score was 67, which was obtained for the Kc-Na-H-60-15 sample. In Set-2 (Kc-Na-B), the observed XRD results were similar for the products formed at 60 °C and 70 °C. Again, the reaction time has only a minor effect on the formation of santite product formed at these temperatures. The XRD scores decreased upon increasing the reaction temperature and time, which was similar to that observed with Set-1.

Table 1. The XRD scores obtained for the synthesized potassium borate products

Reaction Temperature (°C)	Reaction Time (min)	Set-1	Set-2
60	15	67	54
	30	46	55
	60	61	58
	120	60	60
70	15	58	67
	30	50	58
	60	54	50
	120	41	59
80	15	68	64
	30	54	57
	60	37	57
	120	39	31
90	15	46	48
	30	54	63
	60	36	59
	120	33	64

Figure 1 shows the XRD patterns obtained for the synthesized potassium borate products that displayed the higher XRD scores. The characteristic peaks [h k l (d_{spacing})] for santite are seen at the 2θ = 14.92° [1 1 1 (5.93 Å)], 15.85° [0 2 0 (5.59 Å)], 25.32° [0 2 2 (3.51 Å)], 26.59° [1 2 2 (3.35 Å)], 32.35° [4 0 0 (2.77 Å)] and 41.52° [4 2 2 (2.17 Å)].

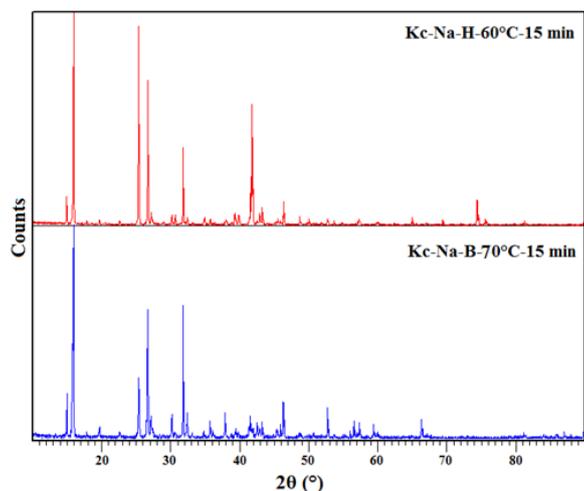


Figure 1. The XRD patterns obtained for the synthesized potassium borate products

3.3. The FT-IR and Raman Spectra Recorded for the Synthesized Potassium Borate Products

The boron atom has two kinds of coordination modes comprised of triangularly coordinated boron atoms (B₍₃₎-O) and tetrahedrally coordinated boron atoms (B₍₄₎-O). The FT-IR spectra recorded for the optimum potassium borate products in both sets are shown in Figure 2. The first characteristic peak was observed in the range of 1332–1425 cm⁻¹ and attributed to the asymmetric stretching of B₍₄₎-O. The bending mode of B-O-H corresponds to the peak observed at 1248 cm⁻¹. The characteristic band observed in the range of 1096–1022 cm⁻¹ was attributed to the asymmetric stretching of B₍₄₎-O. The symmetric stretching band of B₍₃₎-O was observed at ~915 cm⁻¹, whereas the symmetric stretching band of B₍₃₎-O was observed in the range of 781–734 cm⁻¹. The last characteristic vibration bands observed between 693–667 cm⁻¹ were attributed to the bending of B₍₃₎-O.

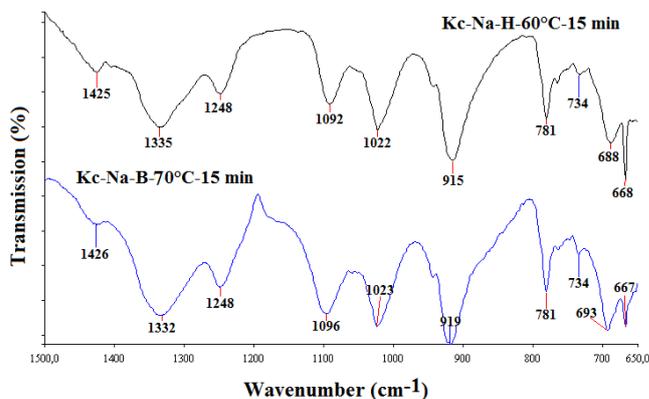


Figure 2. The FT-IR spectra recorded for the optimum synthesized potassium borate products

Raman spectra recorded for the optimum potassium borate products in both sets are given in Figure 3. In the Raman spectra, the band at ~917 cm⁻¹ was attributed to the symmetric stretching of B₍₃₎-O. The symmetric stretching of B₍₄₎-O was observed at 765 cm⁻¹. The peak observed at ~556 cm⁻¹ was attributed to the symmetric vibration of the pentaborate anion ((B₅O₆(OH)₄)⁻). The peaks observed in the range of 509–296 cm⁻¹ were attributed to the bending of B₍₄₎-O.

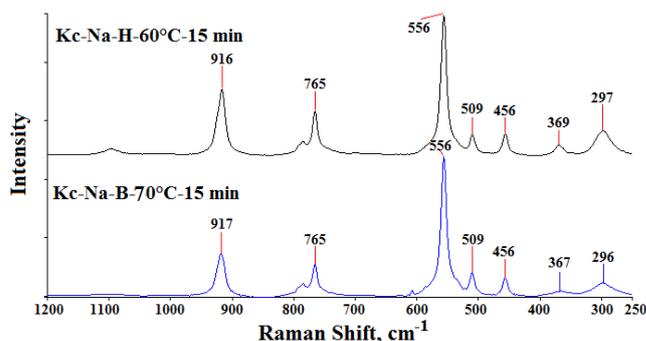


Figure 3. The Raman spectra recorded for the optimum synthesized potassium borate products

The characteristic band values obtained in the analyses were in accordance with the results obtained by Jun et al. and Yongzhong et al. [14, 15].

3.4. The morphologies of the synthesized potassium borate products

The morphologies of the optimum potassium borate products are presented in Figure 4. In Set-1 (Kc-Na-H), the samples were layered and comprised of round-edged particles. The particle sizes varied in the range of 407 nm–2.54 µm. The samples in Set-2 (Kc-Na-B) were comprised of smaller particles when compared with the samples in Set-1. The samples were angular aggregates with particle sizes in the range of 356 nm–2.09 µm.

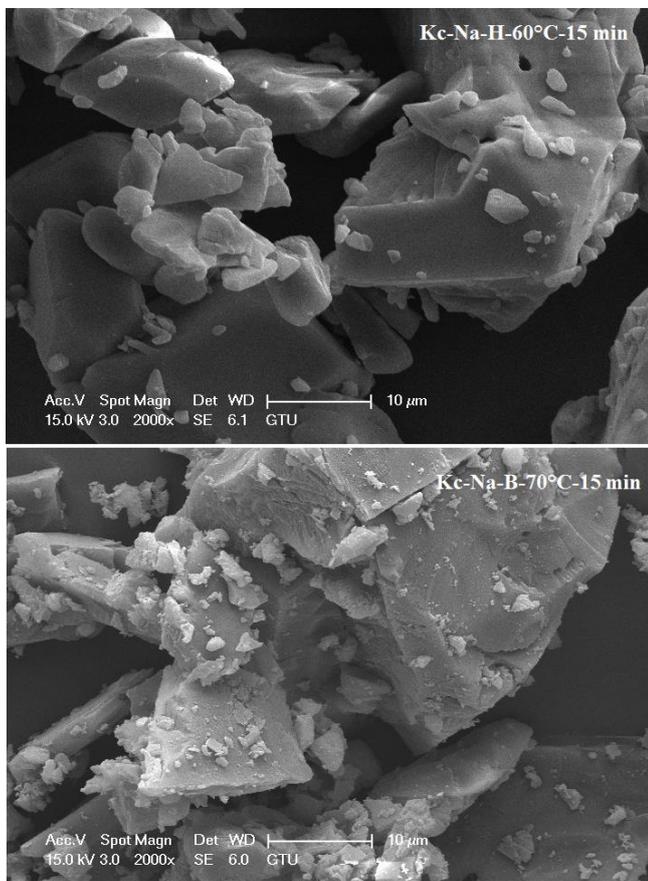


Figure 4. The morphologies of the optimum synthesized potassium borate products

3.5. Reaction yield

The reaction yields were interpreted in accordance with the changing reaction conditions (time and temperature). A three-dimensional surface plot was drawn using the Statistica 8.0 computer program (StatSoft Inc., Tulsa, USA). In the plot, the x-axis represents the reaction temperature (°C), the y-axis represents the reaction yield (%) and the z-axis represents the reaction time (h). The reaction yields obtained for both sets are shown in Figure 5. According to the surface plot, the reaction yield varied in the range of 75.01–95.03% and 72.04–92.22% for Set-1 and Set-2, respectively. Higher

reaction yields were observed at higher reaction temperatures and times. Samples Kc-Na-H-90-120 and Kc-Na-B-90-120 have the highest reaction yields in each set.

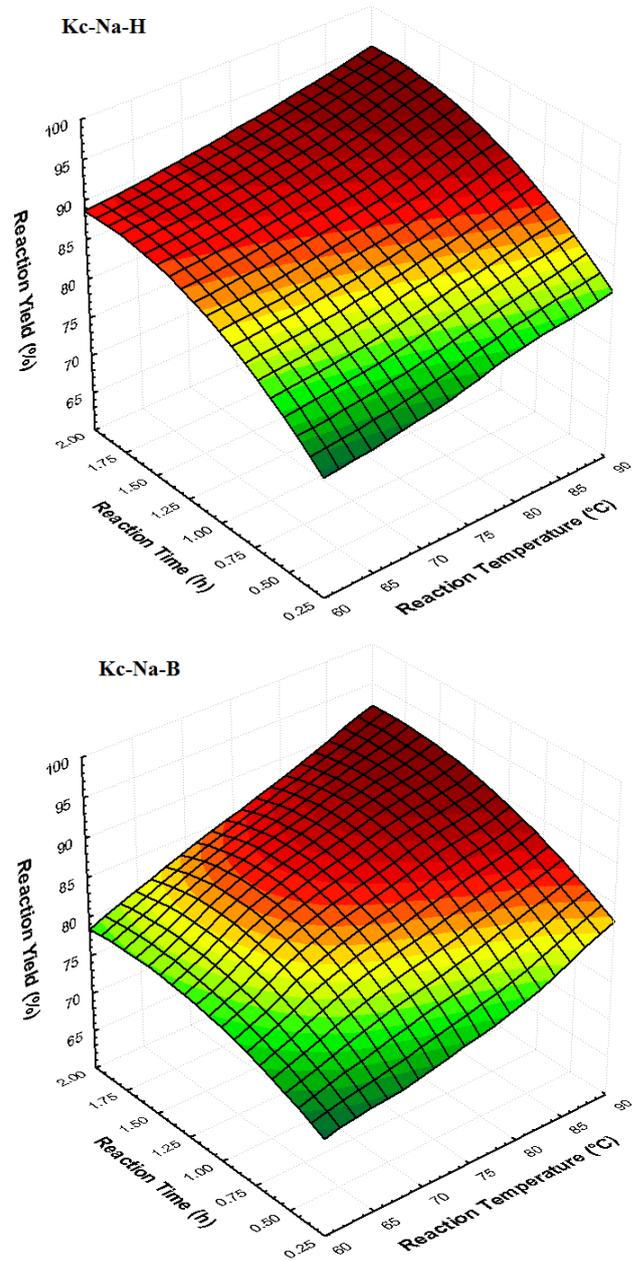


Figure 5. The reaction yields of the synthesized potassium borate products

4. CONCLUSIONS

In the present study, the synthesis of potassium borate hydrate was achieved under moderate reactions conditions when compared to those reported in the literature. The objective of the experiments was to investigate the effects of the reaction conditions on the synthesis of potassium borate hydrate. The results indicated potassium borate hydrate can be prepared using milder reaction reactions (lower temperature (60–90 °C) and shorter time (15–120 min)). The

synthesis of metal borates using a less complex process will help contribute to the use of borates in industrial applications.

The synthesized potassium borate hydrate was identified as santite ($\text{KB}_5\text{O}_8 \cdot 4\text{H}_2\text{O}$). According to the XRD results, higher XRD scores were obtained upon decreasing the reaction temperature. The characteristic band values of boron and oxygen were investigated using FT-IR and Raman spectroscopy. The as-obtained spectra were in good agreement with the literature. The morphologies of the samples were characterized using SEM with both angular agglomerates and round-edged particles observed on the micro-scale. The reaction yields were in the range of 72.04–95.03%.

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