

Synthesis of Trimethyl Borate from Barium Perborate with Nitric Acid as Leaching Agent

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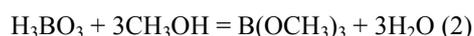
Abstract—Borohydrides are promising materials for hydrogen storage, however, their dehydrogenation process via hydrolysis reaction generates aqueous solution with high boron concentration. Chemical oxo-precipitation process has been demonstrated to recover boron as barium perborate crystals from aqueous solution. In order to fulfill the cycle of borohydrides, this work developed a leaching esterification process to synthesize trimethyl borate (TMB), a precursor of NaBH₄, from barium perborate crystal. Nitric acid was added as a leaching agent during the esterification reaction between barium perborate and methanol to promote the dissolution of boron by precipitation of barium nitrate. The dissolution ratio depended on the dosage of nitric acid, while the yield of TMB was affected by the levels of methanol and water. Under optimal conditions (barium perborate = 5 g, [HNO₃]/[Ba] = 2, [CH₃OH]/[B] = 16, esterification for 4 h and distillation for 1 h), 97.6% of boron was leached out and 77.7% of boron was converted to TMB.

Keywords—Trimethyl borate; Esterification; Leaching; Barium perborate; Barium nitrate

I. INTRODUCTION

Polymer electrolyte fuel cells (PEMFCs) that use hydrogen and air as fuels show great potentials on portable and mobile applications due to their high efficiency and power density, easy operations and safety [1]. However, the hydrogen-related obstacles, especially storages of hydrogen, hindered the wide commercialization of PEMFCs. Boron-based hydrides (BBMs), such as NaBH₄, NH₃BH₃ and N₂H₄BH₃, are attractive chemical hydrogen storage materials owing to their high storage density and capacity [2]. Generally, BBMs release the stored hydrogen by hydrolysis reactions in aqueous solution at the presence of transition metal catalyst [3, 4] and leave the boron in aqueous phase as the form of B(OH)₄⁻ or precipitate as sodium metaborate (NaBO₂) [5, 6].

The cost is a major demerit that restricts the applications of BBMs. Researchers have been devoted to regeneration of BBMs from their by-products. Many studies have been conducted to recycle NaBO₂ directly back to NaBH₄ by reduction using H₂ and Mg at high temperature and pressure [7] or MgH₂ with high-energy ball milling [8]. Another multi-steps method was proposed to recycle NaBO₂, which involves the crystallization of B(OH)₃ (Eq. 1), synthesis of trimethyl borate (TMB) (Eq. 2) and synthesis of NaBH₄ by industrial Brown–Schlesinger process (Eq. 3) [6].



However, little literature has been done on recovery of boron from aqueous solution as the precursor of BBMs.

Chemical oxo-precipitation (COP) process has been demonstrated to recover boron efficiently from aqueous phase as barium perborate (BaB(OH)₂(OO)₂B(OH)₂) at room temperature [9]. The perborate salts, once served as domestic detergents in late 20th century, have never been reported as materials for boron hydrides. Therefore, the goal of this work is to develop a feasible and economic process to convert barium perborate into TMB, a precursor of NaBH₄. This alternative route would provide a new route for the boron cycle of BBMs.

II. MATERIALS AND METHODS

A. Materials

Barium perborate was synthesized by COP process at room temperature. All reagents were analytic grade and used without further purification. Synthetic wastewater was prepared by boric acid (B(OH)₃, Showa). Hydrogen peroxide (H₂O₂, Showa) and barium chloride (BaCl₂·2H₂O) were used as pretreat agent and precipitant, respectively. Synthetic wastewater was mixed with H₂O₂ at molar ratio [H₂O₂]/[B] of 2 and the pH of the mixture was controlled at 10.5 for 20 minutes. Barium solution with the same volume as boron solution was added to generate molar ratio [Ba]/[B] at 0.75 in order to initiate the precipitation process. The reaction proceeded for 4 hours and the pH of the solution was fixed at 10. The barium perborate crystals were collected by 0.45 μm filter (Advantac) and dried at 60 °C for 24 hours. In order to determine the composition of barium perborate, 0.2 g barium perborate crystals were dissolved in 50 ml of 5 wt% HNO₃ solution, then both boron and barium concentration of the solution were quantified by an inductively coupled plasma optical emission spectrometer (ICP-OES, ULTIMA 2000, HORIDA). The results showed that barium perborate comprises 6.23 wt% boron and 48.23 wt% barium.

As for esterification, barium perborate was used as acid and methanol with low water content (CH₃OH, H₂O < 30 ppm,

Showa) as alcohol. Nitric acid (70 wt%, Merck) was used as a leaching agent.

B. Methods

The synthesis of TMB can be divided to two steps: esterification and distillation. For esterification, 5 g barium perborate was mixed with various dosage of nitric acid and methanol, and the mixture was heated at reflux temperature for specific reaction time. After the esterification step was finished, the mixture was distilled at 80 °C to collect distillate. The collected distillate was analyzed by a GC-FID using a DB-5 column to quantify the concentration of TMB and it was also analyzed by ICP-OES to determine the concentration of total boron. The residual solids after the distillation were collected, rinsed by methanol and dried at 60 °C for 24 hours. Afterwards, the composition of the residual solids was analyzed by the same method as barium perborate crystals. The dissolution ratio was calculated by the composition of the residual solids based on the assumption that all of barium remained in solid phase rather than distillate. The yields of TMB were the average of the yields of GC-FID and ICP-OES to minimize experimental errors.

III. RESULTS AND DISCUSSION

A. Leaching effect of nitric acid

The reported TMB processes involves a homogeneous esterification reaction between boric acid and methanol. However, barium perborate ($\text{BaB}(\text{OH})_2(\text{OO})_2\text{B}(\text{OH})_2$) is an ionic solid comprised by barium cation and cyclic perborate anion whose solubility in organic solvent is very poor, including methanol. As shown in Fig. 1, both dissolution ratio and yield of TMB using only barium perborate and methanol were 7.9% and 2.4%, respectively. The esterification reactions between barium perborate and methanol were heterogeneous, so little perborate dissolved into methanol and converted to boric acid and further underwent reactions.

In order to enhance both dissolution ratio and yield of TMB, nitric acid was used as a leaching agent. According to Fig. 1, the addition of nitric acid significantly improved the efficiency of esterification. Nearly 100 percent of boron was leached out as

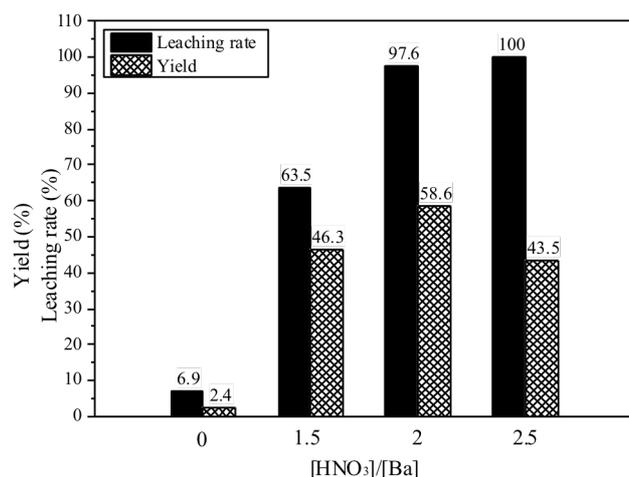
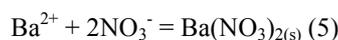
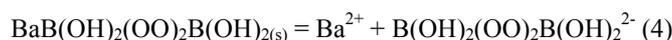


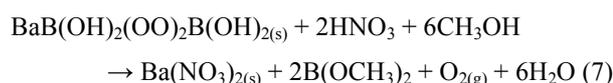
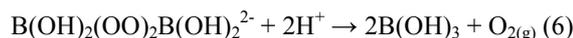
Fig. 1 Effects of dosage of nitric acid as a leaching agent. (Barium perborate = 5 g, $[\text{CH}_3\text{OH}]/[\text{B}] = 12$, esterification for 16 h., distillation for 1 h.)

molar ratio $[\text{HNO}_3]/[\text{Ba}]$ increased higher than 2 and the yield of TMB achieved about 60% with $[\text{HNO}_3]/[\text{Ba}]$ at 2. Although the insoluble solids had been observed throughout esterification, the residual solids were characterized to be majorly barium nitrate ($\text{Ba}(\text{NO}_3)_2$). As shown in Fig. 2, the XRD patterns of residual solids fitted the standard of $\text{Ba}(\text{NO}_3)_2$ (PDF#04-0773) of JCPDF database.

The prominent leaching effect of nitric acid was attributed by the continuous consumption of barium ion in the solution due to the precipitation of $\text{Ba}(\text{NO}_3)_2$. The dissolution of barium perborate is presented as Eq. 4. When abundant nitrate presented in the solution, the barium cation dissolved from barium perborate kept precipitating with nitrate anion as barium nitrate. Based on Le Chatelier's principle, the perborate anion would continuously dissolve out due to insufficient barium level. Therefore, the nitric acid could leach the boron efficiently from barium perborate owing to the common ion effect.



The leached perborate is unstable under the reflux temperature around 65 °C. The perborate released its active oxygen (peroxy bond) and decomposed to boric acid and oxygen gas at the presence of protons (Eq. 6). Furthermore, boric acid reacted with methanol to form TMB (Eq. 2). The overall reactions for esterification of barium perborate at the presence of nitric acid can be described as Eq. 7.



With sufficient dosage of nitric acid ($[\text{HNO}_3]/[\text{Ba}] > 2$), the boron was leached out efficiently. However, the yield of TMB was hindered by over dosage of nitric acid. Because the added nitric acid contained 30% of water, the equilibrium state of TMB is highly affected by the presence of water (Eq. 2). Hence, the optimal dosage of nitric acid is the theoretic dosage of $[\text{HNO}_3]/[\text{Ba}]$ at 2 to capture barium as $\text{Ba}(\text{NO}_3)_2$ efficiently and

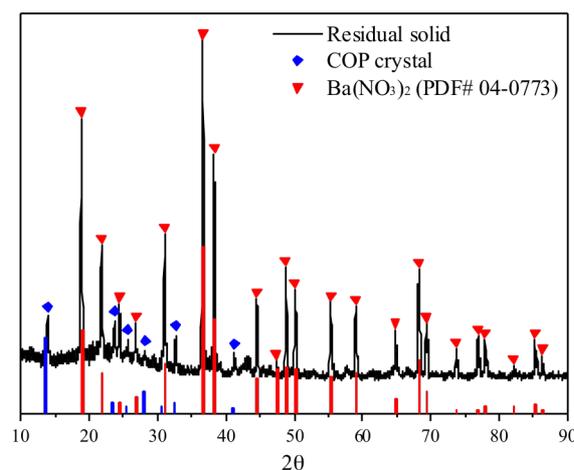


Fig. 2 XRD patterns of the residual solid.

maintain the least water content in the system to achieve higher TMB yield.

B. Effects of reaction time and methanol dosage

This section optimizes the synthesis of TMB from barium perborate with various reaction time and methanol dosage. The mole ratios of $[\text{HNO}_3]/[\text{Ba}]$ were fixed at 2 to obtain the optimal boron dissolution ratio and TMB yield.

Figure 3 shows that the boron dissolution ratios were above 95% as the esterification time increased to longer than 4 hours. The maximum yield of TMB occurred at esterification time of 4 hours. This result may arise from the formation of water. According to Eq. 2 and 7, 3 moles of water are generated as 1 mole of TMB forms, so the content of water increases as more TMB forms. Although more TMB might have form with longer esterification time, the level of water increased simultaneously which might drive the equilibrium of TMB with boric acid and methanol backwards and lead to lower yield of TMB. Hence, the optimal esterification time was 4 hour and the yield of TMB could achieve 68%.

The dosage of methanol was investigated for higher TMB yields. As presented in Fig. 4, the yields of TMB remarkably increased as the mole ratio $[\text{CH}_3\text{OH}]/[\text{B}]$ increased. Although Eq. 2 indicates that boric acid requires only 3 equal moles of methanol to form TMB, the azeotrope between methanol and TMB should take into consideration. At 101.3 kPa, while the boiling points of TMB and methanol are 65 °C and 68 °C, respectively, an azeotrope mixture containing 77% of TMB by weight or 51.3% of TMB by mole boils at 55 °C [6, 10]. Therefore, the esterification of TMB from boric acid and methanol should be rewritten as Eq. 8, indicating that the formation of one mole TMB requires 4 moles of methanol (3 moles for esterification, 1 mole for azeotrope). The theoretical mole ratio $[\text{CH}_3\text{OH}]/[\text{B}]$ is supposed to be 4.



As $[\text{CH}_3\text{OH}]/[\text{B}]$ increased, the formation of TMB in Eq. 8 was favored. However, the distillate contained large amount of

methanol. Further purification of distillate is required and excess methanol can be recycled and reused.

IV. CONCLUSION

The synthesis of TMB from barium perborate was developed for the boron cycle of borohydrides. Barium perborate crystals are the by-products reclaimed from concentrated boron solution by the means of chemical oxo-precipitation (COP). The addition of nitric acid significantly enhanced the dissolution ratio of boron by precipitating soluble barium as barium nitrate and promoted the dissolution of barium perborate in methanol solution. Furthermore, the equilibrium between boron, methanol and water dominated the yield of TMB. The yields increased as the dosage of methanol increased and the level of water decreased. Under optimal conditions (barium perborate = 5 g, $[\text{HNO}_3]/[\text{Ba}] = 2$, $[\text{CH}_3\text{OH}]/[\text{B}] = 16$, esterification for 4 h and distillation for 1 h), 97.6% of boron was leached out and 77.7% of boron was converted to TMB.

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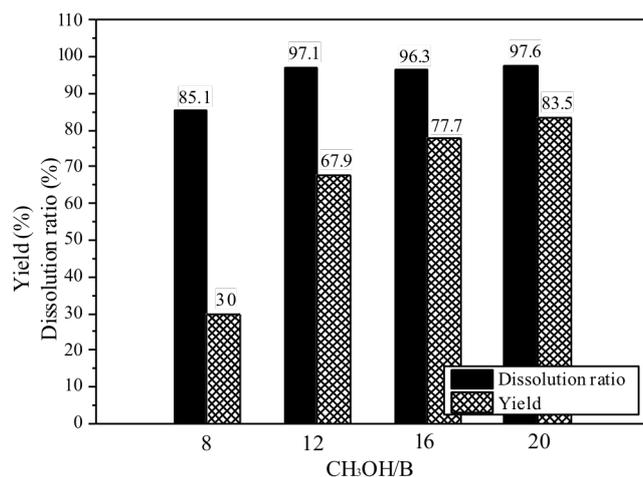


Fig. 4 Effect of dosage of methanol on the dissolution ratio and TMB yield. (Barium perborate = 5 g, $[\text{HNO}_3]/[\text{Ba}] = 2$, esterification for 4 h and distillation for 1 h.)