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TÜRKİYE CUMHURİYETİ'NİN
YÜZ BİRİNCİ YILI



Investigation of Sodium Borohydride Synthesis from Anhydrous Borax: Impact of Stoichiometry and Alternative Reducing Agents

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Abstract: The production of sodium borohydride from anhydrous borax using aluminum and sodium hydroxide as reactants was investigated in a bomb-type batch reactor under hydrogen atmosphere. The study evaluated the effects of stoichiometric ratios and the addition of calcium carbide on yield and product composition. Experiments without calcium carbide, employing 100% molar excess of aluminum and sodium hydroxide, increased the yield from 11.31% to 13.28%. However, incorporating calcium carbide redirected the reaction mechanism, leading to the formation of complex phase structures. Structural characterization using FT-IR and XRD confirmed the consistency of products from Experiments 1 and 2 with reference NaBH₄. In contrast, products from Experiments 3, 4 and 5 showed significant deviations, with no NaBH₄-specific peaks observed. These findings underscore the importance of stoichiometric optimization and particle size reduction (<150 μm) for improving reaction efficiency. Future studies should focus on refining process parameters and understanding the role of alternative reducing agent.

Keywords: Sodium borohydride, anhydrous borax, calcium carbide

Susuz Borakstan Sodyum Borhidrür Sentezi: Stokiyometri ve Alternatif İndirgeyici Malzemelerin Etkisi

Öz: Susuz borakstan, alüminyum ve sodyum hidroksit kullanılarak sodyum borhidrür üretimi, hidrojen atmosferinde çalışan bomba tipi kesikli bir reaktörde incelenmiştir. Çalışmada, stokiyometrik oranların ve kalsiyum karbür ilavesinin verim ve ürün kompozisyonu üzerindeki etkileri değerlendirilmiştir. Kalsiyum karbür kullanılmayan deneylerde, molce %100 fazla alüminyum ve sodyum hidroksit kullanımı reaksiyon verimini %11.31' den %13.28' e çıkarmıştır. Ancak, kalsiyum karbür ilavesi reaksiyon mekanizmasını değiştirerek, kompleks faz yapılarının oluşumuna yol açmıştır. FT-IR ve XRD ile yapılan yapısal karakterizasyon, 1 ve 2 numaralı deneylerde elde edilen ürünlerin referans NaBH₄ ile uyumlu olduğunu doğrulamıştır. Buna karşın, 3, 4 ve 5 numaralı deneylerin ürünleri, NaBH₄'e özgü piklerin gözlemlenmediği önemli farklılıklar göstermiştir. Bu bulgular, reaksiyon verimliliğinin artırılmasında stokiyometrik optimizasyonun ve tanecik boyutunun küçültülmesinin (<150 μm) önemini vurgulamaktadır. Gelecek çalışmalar, proses parametrelerinin iyileştirilmesine ve alternatif indirgeme ajanlarının rolünün anlaşılmasına odaklanmalıdır.

Anahtar Kelimeler: Sodyum borhidrür, susuz boraks, kalsiyum karbür

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Introduction

The increasing demand for sustainable and clean energy sources has intensified research into hydrogen-based energy systems. Among various hydrogen storage materials, sodium borohydride (NaBH_4) stands out due to its high hydrogen content, chemical stability and ability to generate hydrogen efficiently through hydrolysis. (Demirci & Miele, 2009; Santos & Sequeira, 2011; Amendola et al., 2000). This unique reaction, which produces hydrogen gas and sodium metaborate, offers a safe and clean method for hydrogen generation under moderate conditions, making NaBH_4 an appealing candidate for portable and stationary energy applications (Kojima et al., 2002; Brack et al., 2015). Moreover, in hydrogen fuel cells, it contributes to systems that yield water as the sole by-product, aligning with global goals for eco-friendly energy solutions (Marrero-Alfonso et al., 2007; Kong et al., 2009).

Despite its clear advantages, the widespread adoption of NaBH_4 has been significantly limited by challenges in its production and regeneration. The traditional Brown-Schlesinger process, widely used for industrial synthesis, requires high temperatures, pressures and costly raw materials such as sodium hydride (Schlesinger et al., 1953). This method is energy-intensive, complex and results in the formation of various by-products. Meanwhile, the Bayer process, which employs borates and metallic sodium in high-pressure hydrogen environments, offers a direct route to NaBH_4 but presents its own set of difficulties, including by-product management and operational risks (Demirci, 2015; Demirci et al., 2017).

Researchers have directed significant efforts toward overcoming these challenges, focusing heavily on improving the hydrolysis process of NaBH_4 to optimize hydrogen generation (Amendola et al., 2000; Demirci & Miele, 2009; Santos & Sequeira, 2011). However, a significant gap exists in research dedicated to regenerating NaBH_4 from its hydrolysis by-products. Efforts to address this gap have led to the development of three primary methods for NaBH_4 production: thermochemical, mechano-chemical and electrochemical approaches. Thermochemical methods, relying on high-temperature reactions, have demonstrated high yields, particularly when magnesium hydride is used as a reducing agent (Kojima et al., 2002; Nunes et al., 2021). However, these methods are energy-intensive and costly. Mechano-chemical techniques, such as ball milling, present an environmentally friendly alternative by utilizing mechanical energy to drive reactions (Kong et al., 2009; Çakanyıldırım & Gürü, 2011). While these methods avoid the need for high temperatures, they often require extended processing times, limiting their industrial scalability (Marrero-Alfonso et al., 2007). Electrochemical regeneration, a newer approach, offers a cleaner and potentially more efficient pathway for NaBH_4 synthesis. Recent studies have demonstrated its feasibility, though challenges such as competing side reactions and low efficiencies continue to hinder its widespread application (Nunes et al., 2021).

An area of significant interest in NaBH_4 production and regeneration is the choice of reducing agents. Studies have highlighted the impact of different reducing materials on yield, efficiency and cost. Magnesium hydride (MgH_2) is frequently used due to its high reactivity, but its expense has driven research into alternatives like magnesium, aluminum and silicon-based compounds (Eom et al., 2013; Figen & Piskin, 2013; Ou et al., 2013). On the other hand, silicon-based reducing agents, while less reactive, offer a more cost-effective solution, particularly in mechano-chemical processes. The incorporation of alloying elements such as nickel with magnesium has also been shown to enhance reaction kinetics and improve yield by facilitating hydrogen dissociation (Nunes et al., 2021). Additionally, the use of hydrated borates in regeneration processes has gained traction, as studies have demonstrated that these materials can achieve comparable yields to their anhydrous counterparts while avoiding the energy-intensive dehydration step (Marrero-Alfonso et al., 2007). The choice of reducing agents thus remains a critical factor in optimizing NaBH_4 production, balancing cost, efficiency and environmental considerations.

Sodium borohydride holds great potential as a hydrogen carrier, but its full integration into energy systems depends on overcoming the economic and technical challenges associated with its production and regeneration. Continued innovation in the use of reducing agents, coupled with advancements in process efficiency and scalability, will be key to unlocking the widespread adoption of NaBH_4 in the hydrogen economy. By addressing these challenges, NaBH_4 can become a cornerstone of sustainable energy technologies, contributing to a cleaner and more sustainable future.

Recent studies have explored various pathways to optimize NaBH_4 synthesis, focusing on reducing agent selection, reaction mechanisms and process conditions. The use of alternative reducing agents, such as magnesium has shown potential in improving reaction efficiency and reducing costs. Additionally, advancements in mechanochemical and thermochemical synthesis techniques have opened new avenues for enhancing the feasibility of NaBH_4 production. However, the role of stoichiometric ratios, reaction pathways and alternative reactants in maximizing yield and minimizing by-products remains underexplored.

This study aims to address these gaps by investigating the production of NaBH_4 from anhydrous borax using aluminum and sodium hydroxide as key reactants in a bomb-type batch reactor. The effects of stoichiometric variations, particularly the use of molar excess aluminum and sodium hydroxide, are examined to optimize the reaction yield. Furthermore, the impact of incorporating calcium carbide as an additional reducing agent is evaluated to understand its influence on the reaction mechanism and product composition. Structural characterization using X-ray diffraction (XRD) and Fourier-transform infrared (FT-IR) spectroscopy provides insights into the phases and functional groups of the synthesized products.

Materials and Methods

Materials

$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (borax decahydrate) was obtained from Bandırma Eti Bor Tesisleri and used as the primary boron source in the experiments. Aluminum (Al , $\geq 99\%$) was purchased from Sigma-Aldrich, while high-purity SiO_2 (70–230 mesh) was also sourced from Sigma-Aldrich. NaOH (sodium hydroxide, $\geq 99\%$) was procured from Merck. Sodium metaborate tetrahydrate ($\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$, $\geq 99\%$) was obtained from Sigma-Aldrich. Ethanol ($\text{C}_2\text{H}_5\text{OH}$, $\geq 99.9\%$) was supplied by Isolab Chemicals. Sodium borohydride (NaBH_4 , reference material, $\geq 99.9\%$) was sourced from AFG Scientific. Other reagents included H_2SO_4 (sulfuric acid, 95–98%) from Merck, KIO_3 (potassium iodate, $\geq 99.9\%$) from Merck, $\text{Na}_2\text{S}_2\text{O}_3$ (sodium thiosulfate, $\geq 99.9\%$) from AFG Scientific and KI (potassium iodide, $\geq 99.9\%$) from Merck. Starch used in titration procedures was purchased from Merck. Calcium carbide (CaC_2) was obtained from Ankaizen Mühendislik.

Methods

Borax decahydrate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) was subjected to calcination to remove the crystalline water in its structure. The calcination temperature and duration were determined based on the thermogravimetric analysis (TGA) data presented in Figure 1 and prior studies in the literature (Gençaslan & Karaduman, 2016; Li et al., 2003). Accordingly, borax decahydrate was calcined at 630°C for 4 hours. The calcined product was then stored in airtight containers within a desiccator to prevent moisture uptake.

The particle size reduction of solid reactants is crucial for increasing surface area, preventing agglomeration and enhancing reaction efficiency. The grinding process for the solid reactants was conducted using a vibration ball mill located at the Çanakkale Onsekiz Mart University Science and Technology Application and Research Center. The ground solid materials were then sieved using a shaking sieve device, also located at the same facility, to ensure a uniform particle size of ≤ 150 microns. The sieved powders were subsequently stored in airtight containers to preserve their properties and prevent contamination.

A laboratory-scale stainless steel bomb-type reactor with an internal diameter of 200 cm^3 was utilized for sodium borohydride production experiments. The reactor was heated using a high-temperature crucible furnace system, capable of operating up to 1000°C , with the reactor's lower section fully submerged within the furnace chamber to ensure uniform thermal distribution.

The sodium borohydride production experiments were conducted using the system schematically illustrated in Figure 2. The system included the following components: (1) a high-purity hydrogen cylinder serving as the gas source, (2) a high-pressure-resistant gas delivery line for the safe transfer of hydrogen, (3) a high-pressure-resistant needle valve for precise gas flow control, (4) a manometer to monitor the internal gas pressure of the reactor, (5) a thermocouple for measuring the temperature within the system, (6) a temperature control unit for accurate thermal regulation, (7) a crucible-type heating unit to provide the required thermal energy, (8) a bomb-type stainless steel batch reactor capable of withstanding high pressures and temperatures and (9) a custom-designed hydrogen regulator to facilitate the controlled inlet and outlet of hydrogen gas at high pressures.

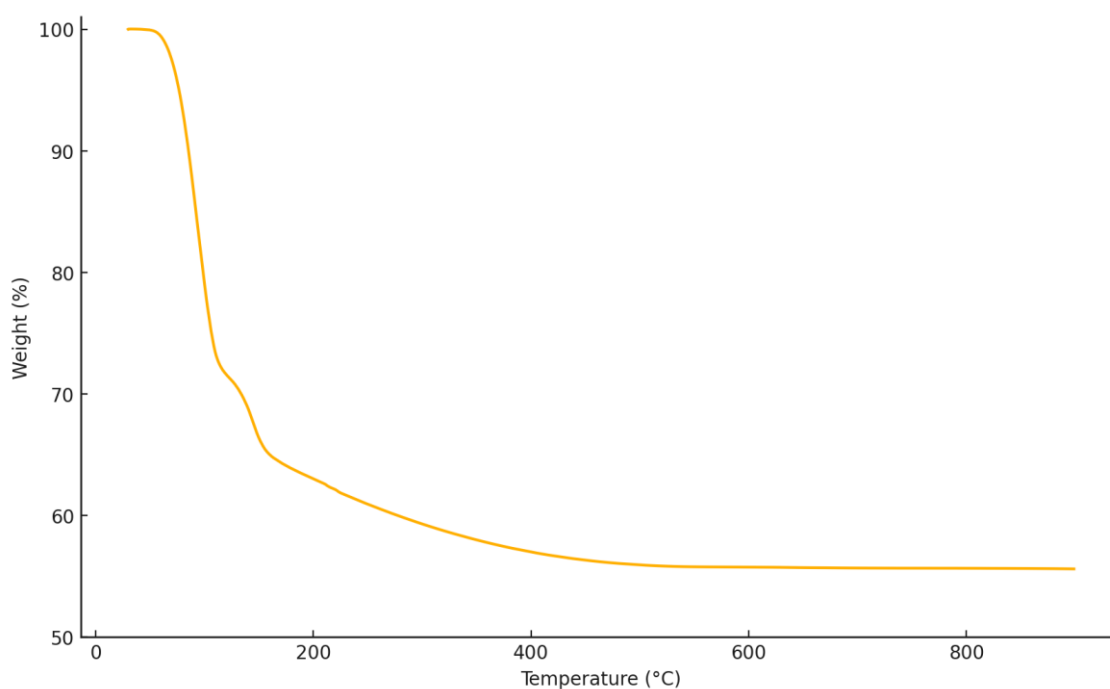


Figure 1. Result of Thermogravimetric Analysis (TGA) of Borax Decahydrate

The study investigated how the stoichiometric ratios of aluminum (Al) as the reducing agent, sodium hydroxide (NaOH) as the sodium source and the addition of calcium carbide (CaC_2) as an extra reducing agent affected the yield of sodium borohydride. The amounts of the reactants used in the reaction were given in Table 1. The reactants were thoroughly mixed before being transferred into the reactor. To prevent any oxygenation reactions during the process, the reactor was degassed for several times using nitrogen gas. Following this, hydrogen was introduced into the reactor with 20 bar initial pressure. The reactor was then positioned in the furnace. It was subsequently heated to 450°C and maintained at this temperature for 4 hours.

The proposed reaction mechanism for the formation of sodium borohydride from anhydrous borax can be expressed through Equation 1 (Alibeyli et al., 2008; Alibeyli et al., 2011);



Table 1. Experimental Conditions for Sodium Borohydride Production

Experiment No	Temperature (°C)	Initial H ₂ Pressure (bar)	Duration (hours)	Chemicals Used (g)
1	450	20	4	$\text{Na}_2\text{B}_4\text{O}_7$: 5.00 ; Al: 4.04 ; NaOH: 1.99 ; SiO_2 : 1.50
2	450	20	4	$\text{Na}_2\text{B}_4\text{O}_7$: 5.00 ; Al: 8.08 ; NaOH: 3.98 ; SiO_2 : 1.50
3	450	20	4	$\text{Na}_2\text{B}_4\text{O}_7$: 5.00 ; Al: 4.04 ; NaOH: 1.99 ; SiO_2 : 1.50 ; CaC_2 : 1.59
4	450	20	4	$\text{Na}_2\text{B}_4\text{O}_7$: 5.00 ; Al: 8.08 ; NaOH: 3.98 ; SiO_2 : 1.50 ; CaC_2 : 1.59
5	450	20	4	$\text{Na}_2\text{B}_4\text{O}_7$: 5.00 ; Al: 8.08 ; NaOH: 3.98 ; SiO_2 : 1.50 ; CaC_2 : 3.18

The sodium borohydride (SBH) produced was isolated from the solid reaction mixture using ethyl alcohol as the extraction medium. The solvent was then removed under vacuum at 50°C , leaving the solid SBH, which was subsequently separated.

The iodometric method is the most widely used volumetric or titrimetric technique for analyzing borohydride ions (Lytle et al., 1952). In this study, the quantity of borohydride produced was measured using

iodometric titration, conducted at room temperature and under atmospheric pressure. X-Ray Diffraction (XRD) was used for the qualitative characterization of the products. XRD patterns were recorded at room temperature by using PANalytical Empyrean diffractometer with Cu-K α radiation ($\lambda = 1.54060 \text{ \AA}$). The 2θ scan range was from 5.0064° to 79.9904° with a step size of 0.013° and a scan speed of 0.026° per second. The generator was operated at 40 mA and 45 kV. The functional groups within the samples were identified using an Agilent Technologies Cary 630 FT-IR spectrometer, with measurements performed in the range of $4000\text{-}650 \text{ cm}^{-1}$.

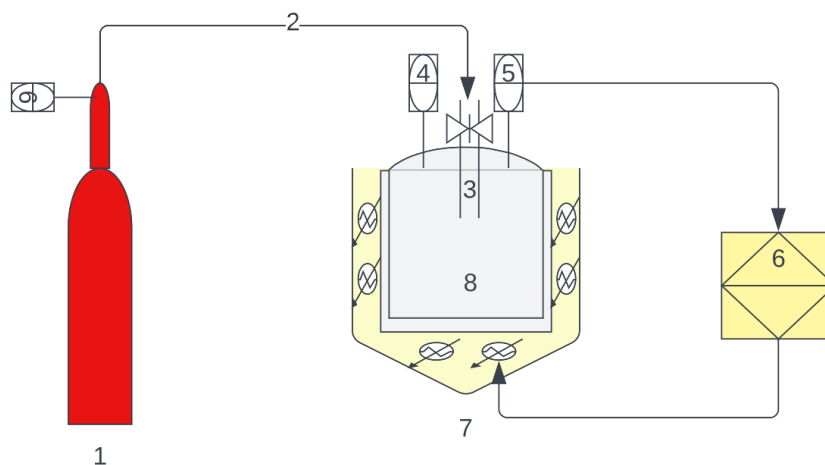


Figure 2. System Scheme for Sodium Borohydride Production

Results and Discussion

The sodium borohydride production process, utilizing anhydrous borax ($\text{Na}_2\text{B}_4\text{O}_7$) as the boron source, aluminum metal as the reducing agent and sodium hydroxide as the sodium source, was conducted in a bomb-type batch reactor operating under a hydrogen atmosphere. The reactor was operated at 450°C , with an initial H_2 pressure of 20 atm and a reaction time of 4 hours. The study was extended under the same conditions, adding different amounts of calcium carbide as the reducing agent. The experimental results showed that the conversion rate of anhydrous borax to sodium borohydride was 11.31% in Exp. No 1 and 13.28% in Exp. No 2, where an excess of aluminum and sodium hydroxide (100% molar excess) was used. Additionally, the effects of incorporating various amounts of calcium carbide into the sodium borohydride synthesis reaction conditions were investigated (Exp. No 3, 4 and 5). The results suggest that calcium carbide redirects the reaction mechanism away from sodium borohydride production towards a different reaction pathway. However, the full extent and nature of this effect and interaction could not be fully determined.

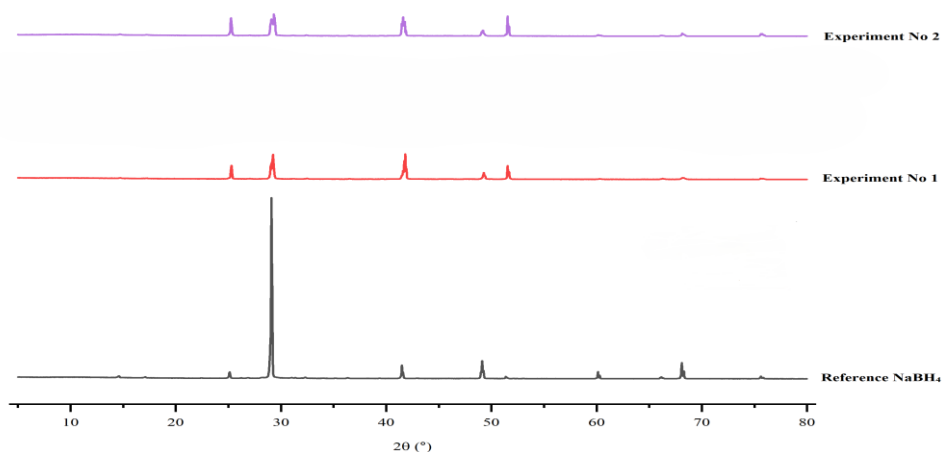


Figure 3. Comparative XRD Diagrams of Products from Experiment No 1 and 2

Sodium borohydride (NaBH_4) obtained from the solid products of Experiments 1 and 2 was extracted using ethanol. Following this extraction process, X-ray diffraction (XRD) analysis was performed on the resulting samples. Based on the XRD results, the crystal structure was found to be fully consistent with sodium borohydride (PDF: 00-078-0544) (Figure 3). Comparative analysis of the XRD patterns of the sodium borohydride samples revealed that the characteristic peaks occurred at similar diffraction angles. Additionally, the main products obtained after extraction were white in color and exhibited the distinctive odor of sodium borohydride. These findings confirm that the compounds obtained are indeed sodium borohydride.

The solid products obtained from Experiments 3, 4 and 5, conducted using varying amounts of calcium carbide starting from anhydrous borax, were analyzed via X-ray diffraction (XRD). Based on the XRD results, multiple peaks with diffraction angles different from sodium borohydride were observed (Figure 4). It is hypothesized that a complex phase structure formed as a result of the combination of various compounds during the reaction. The XRD analysis, supported by database searches from the instrument's library, identified potential phases in the products, including unreacted aluminum (PDF: 00-089-2837), calcium hydroxide (PDF: 00-084-1263), sodium borate (PDF: 00-022-1344) and boron carbide (PDF: 00-075-0424). The resulting products were white in color and the characteristic odor of sodium borohydride was not detected. These findings indicate that the reaction mechanisms in these experiments diverted from the path leading to sodium borohydride formation.

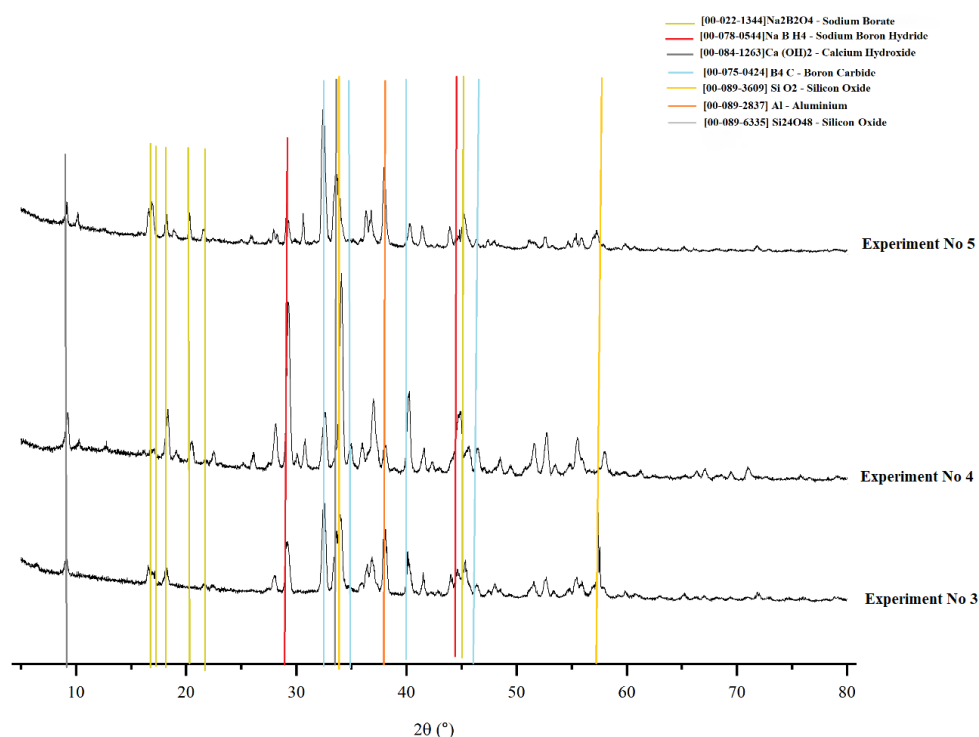


Figure 4. Comparative XRD Diagrams of Products from Experiment No 3, 4 and 5

The functional group structure of the primary product obtained after the separation process from the solid products of Experiments 1, 2, 3, 4 and 5 was analyzed using Fourier Transform Infrared (FT-IR) spectroscopy in the wavenumber range of $4000\text{--}650\text{ cm}^{-1}$. As shown in Figure 5, the FT-IR spectrum for the products of Experiments 1 and 2 revealed vibrational frequencies corresponding to O-H bonds in the $3600\text{--}3465\text{ cm}^{-1}$ range, B-H bonds in the $2270\text{--}2200\text{ cm}^{-1}$ range, B=O bonds in the $1618\text{--}1440\text{ cm}^{-1}$ range and B-O bonds in the $1100\text{--}1050\text{ cm}^{-1}$ range. These results confirm that the obtained compound is consistent with the reference structure of sodium borohydride (NaBH_4). In contrast, the FT-IR spectra of the solid products from Experiments 3, 4 and 5 exhibited peaks significantly different from the reference NaBH_4 . This indicates that the reaction conditions in these experiments led to the formation of compounds with structures distinct from sodium borohydride.

Alibeyli et al. (2011) stated that synthesis conditions significantly affect the yield of NaBH_4 but do not influence its purity. However, their study did not investigate the effect of the stoichiometric ratios of reactants. In

this study, it has been demonstrated that using an excess of NaOH (100% molar excess) and Al (100% molar excess) in the reaction medium is more effective in enhancing the yield.

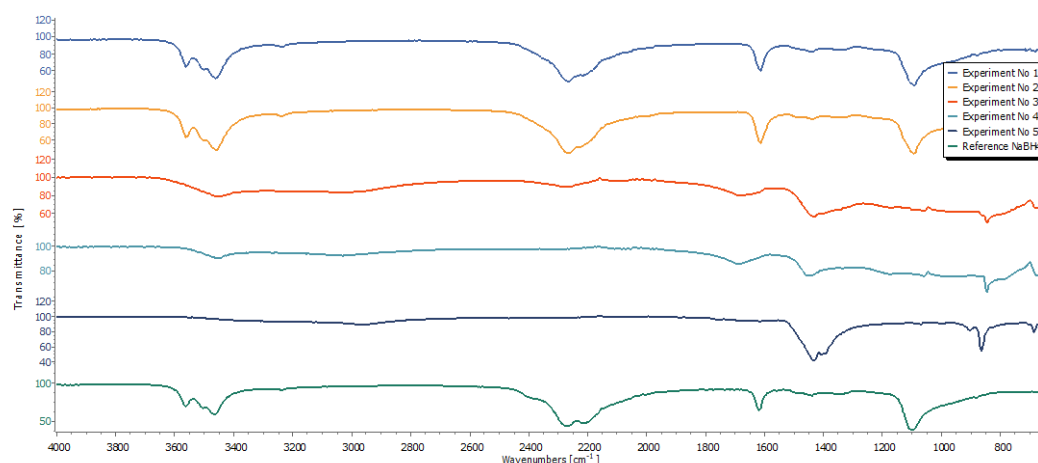


Figure 5. Comparative FT-IR Spectrums of Products from Experiment No 1, 2, 3, 4 and 5

In the study conducted by Gençaslan and Karaduman (2016), the production of sodium borohydride was investigated using $\text{Na}_2\text{B}_4\text{O}_7$ and NaBO_2 . Experiments were carried out in a 45 mL stainless steel vibratory ball mill reactor. A magnesium (Mg)-based method was selected for sodium borohydride production. The experiments were conducted at a temperature of 412°C , an initial hydrogen pressure of 29 atm, a vibration frequency of 10 Hz (600 rpm) and a reaction time of 150 minutes. The yield of sodium borohydride obtained using anhydrous borax was 17.1%, while the yield obtained using sodium metaborate was 17.9%. It was stated that these low yields were due to the reduced contact surface area between Mg and H^- (protid) as a result of the large particle size of the Mg metal ($175\ \mu\text{m}$). It is well-known that the particle size of reactants is crucial in solid-solid reactions, as it significantly affects the contact surface area. Similarly, in this study, one potential reason for the lower conversion rates compared to the literature could be the inability to reduce the particle size below $150\ \mu\text{m}$. This highlights the importance of particle size optimization to improve reaction efficiency in such systems.

Conclusion

This study demonstrated the production of sodium borohydride (NaBH_4) using anhydrous borax as a boron source in a bomb-type batch reactor. It was found that utilizing 100% molar excess of aluminum and sodium hydroxide significantly improved the yield of NaBH_4 , increasing conversion rates from 11.31% to 13.28% in experiments without calcium carbide. Conversely, experiments involving calcium carbide showed a shift in the reaction mechanism, resulting in complex phase structures and compounds such as unreacted aluminum, calcium hydroxide and sodium borate, which diverted from NaBH_4 formation. FT-IR and XRD analyses confirmed the structural consistency of the products from Experiments 1 and 2 with reference NaBH_4 , while products from Experiments 3, 4 and 5 exhibited significant deviations. These findings highlight the critical role of stoichiometric ratios and the choice of reducing agents in optimizing NaBH_4 synthesis. However, the limited particle size reduction ($<150\ \mu\text{m}$) of the reactants likely hindered reaction efficiency, emphasizing the need for further process optimization.


Future research should explore the impact of finer particle sizes, alternative reducing agents and continuous reaction setups to enhance yield and scalability. Additionally, understanding the role of calcium carbide in altering reaction pathways could pave the way for novel compound syntheses in boron chemistry.

Additional Information and Declarations

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