

# NaBH<sub>4</sub> Hydrolysis for Hydrogen Generation over Metal-Organic Frameworks (Cu-BTC)

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Received: 26<sup>th</sup> June 2023 Revised: 19<sup>th</sup> July 2023 Accepted: 29<sup>th</sup> July 2023

Published online: 30<sup>th</sup> July 2023

**Abstract:** Hydrogen gas (H<sub>2</sub>) is widely acknowledged as a sustainable and environmentally friendly energy carrier. In this study, we examined the potential of copper-based metal-organic frameworks (MOFs); copper-benzene-1,3,5-tricarboxylate (Cu-BTC), as catalysts for the release of hydrogen through the hydrolysis of sodium borohydride (NaBH<sub>4</sub>). Cu-BTC exhibited a hydrogen generation rate (HGR) of 4386 mL<sub>H<sub>2</sub></sub> g<sub>cat</sub><sup>-1</sup> min<sup>-1</sup> using low catalyst loading of 1 mg. The effect of the reactant weight percentage of NaBH<sub>4</sub> (0.2-3 wt/wt.) at room temperature was investigated. Thermal analysis of the hydrolysis process revealed that Cu-BTC MOF exhibits low activation energy of 41.7 kJ mol<sup>-1</sup>. The study investigated the recyclability of the catalyst and found that Cu-BTC could sustain the catalyst for hydrogen generation for up to four cycles without any noticeable decline in performance. This research demonstrated that Cu(BTC) is an inexpensive, efficient, and reusable catalyst for generating hydrogen through hydride hydrolysis.

**Keywords:** MOFs, Copper, Hydrogen, Energy, NaBH<sub>4</sub>, climate change.

## 1. Introduction

Energy and environmental pollution can be considered among the topic influencing the quality of life [1, 2]. Green, renewable, and efficient energy resources must be mined urgently [3-11]. Hydrogen is a "green" energy source due to its advantageous characteristics. It has a high energy content of 142 MJ/kg, more than three times as much as gasoline's energy content of 47 MJ/kg, with a friendly byproduct of H<sub>2</sub>O and no CO<sub>2</sub> emissions [12]. Thus, it can mitigate the release of greenhouse gases limiting climate change [13]. The storage and release of hydrogen using solid-state hydride such as sodium borohydride is an effective strategy for several applications e.g., small portable electronics and crewless airplanes [6]. Sodium borohydride (NaBH<sub>4</sub>) contains a significant amount of hydrogen, with a hydrogen content of 10.8 wt. %. This indicates that NaBH<sub>4</sub> is a rich source of hydrogen, making it a valuable material for hydrogen-related applications. Adjustable hydrogen generation rates (HGRs), and suitability for low energy demand applications [14]. The hydrolysis of NaBH<sub>4</sub> can be described as a process similar to "chemical water-splitting." This is because a significant portion of the hydrogen gas released during the reaction is derived from the water molecules present. In other words, the water molecules contribute to the generation of hydrogen gas through their interaction with NaBH<sub>4</sub>. This characteristic of the hydrolysis reaction highlights its potential as a method for producing hydrogen gas by utilizing water as one of the reactants [15-18]. Furthermore, the byproduct of the hydrolysis i.e., sodium metaborate by-product (NaBO<sub>2</sub>·xH<sub>2</sub>O, x

where is the number of hydration water) can be used to regenerate materials into NaBH<sub>4</sub> [11, 19].

The porous, highly surface-area materials known as metal-organic frameworks (MOFs), have large pore sizes, and volumes [20-27]. Numerous uses included medication delivery, sensing, biosensing, adsorption, electronics, and catalysis [28-35]. MOFs have been used as photocatalysts for the evolution of H<sub>2</sub> from water [35]. Therefore, they could be useful materials for NaBH<sub>4</sub> hydrolysis to produce "green" hydrogen gas. Cu-BTC belongs to a class of MOFs and exhibits interesting properties and applications. One of the remarkable features of Cu-BTC is its high porosity [36]. The structure contains large, well-defined pores that can accommodate guest molecules or ions. This porosity provides a large surface area, making Cu-BTC attractive for a variety of uses, including the catalysis, separation, and storage of gases. The porous design allows for the storage and adsorption of gases including hydrogen, methane, carbon dioxide, and even volatile chemical molecules. This property makes Cu-BTC useful for gas storage and purification, as well as selective gas separation processes. Cu-BTC exhibits catalytic properties due to the presence of copper ions. It can act as a catalyst in a variety of chemical processes, including oxidation and reduction reactions. The porous structure provides a high surface area for reactants to interact with the catalytic sites, leading to enhanced reaction rates and selectivity. Cu-BTC can adsorb various organic and inorganic molecules on its surface or within its pores [37]. This property enables its use in applications such as pollutant removal, water purification, and drug delivery systems. The selective

adsorption capabilities of Cu-BTC can be tailored by modifying its structure or incorporating different functional groups. Cu-BTC's unique properties make it valuable in several fields. Some potential applications include gas storage for alternative energy systems, gas separation for industrial processes [38], catalysis for chemical reactions, adsorption for environmental remediation, and drug delivery systems. In recent years, there has been a lot of scientific interest in Cu-BTC and other MOFs. In addition to researching new synthesis techniques and investigating innovative applications, researchers are looking into ways to improve the stability, selectivity, and performance of these materials. The characteristics of Cu-BTC are being optimized, and its application possibilities are being increased.

Here, Cu-BTC was synthesized, characterized, and applied for the hydrolysis of NaBH<sub>4</sub>. The material was characterized using X-ray diffraction (XRD), Fourier transforms infrared spectroscopy (FT-IR), and transmission electron microscopy (TEM). Cu-BTC has a porous crystalline structure comprised of benzene-1,3,5-tricarboxylate and copper ions in a coordinated system of ligands. The copper ions form paddlewheel-like structures connected by the organic ligands, creating a three-dimensional network with large open channels and pores. High catalytic performance was demonstrated by this material. Using a low loading of the Cu-BTC (1 mg) in which the NaBH<sub>4</sub> concentration varies (0.2, 0.5, 1, 2, and 3 wt/wt.) at 25°C. The activation energy is only 41.7 kJ mol<sup>-1</sup>, which is not very high. Cu-BTC MOF showed maximum hydrogen generation rates (HGRs) of 4386 mL<sub>H<sub>2</sub></sub> g<sub>cat</sub><sup>-1</sup> min<sup>-1</sup>. Cu-BTC shows high recyclability which indicates its potential as a sustainable and cost-effective catalyst. The material's ability to maintain its catalytic activity over multiple cycles offers stability, versatility, and reduced environmental impact in various industrial applications.

## 2. Experimental

### 2.1. Materials and Methods

Sigma Aldrich (Germany) provided the following materials: copper nitrate (Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O), benzene-1,3,5-tricarboxylic acid (H<sub>3</sub>BTC), and dimethyl formamide (DMF). We bought NaBH<sub>4</sub> from Fisher Scientific (UK).

### 2.2. Synthesis of Cu-BTC

The hydrothermal synthesis of Cu-BTC [38] involved several steps. Firstly, BTC (234 mmol) and cupric nitrate hydrate (466 mmol) were dissolved in DMF (200 mL). The resulting mixture was then refluxed for ten hours. After the completion of the reaction, the flask was cooled to room temperature, leading to the formation of blue Cu-BTC crystals. The synthesized material was then separated by filtration and washed with DMF and water to remove any impurities or residual reactants.

### 2.3. Instruments for Characterization

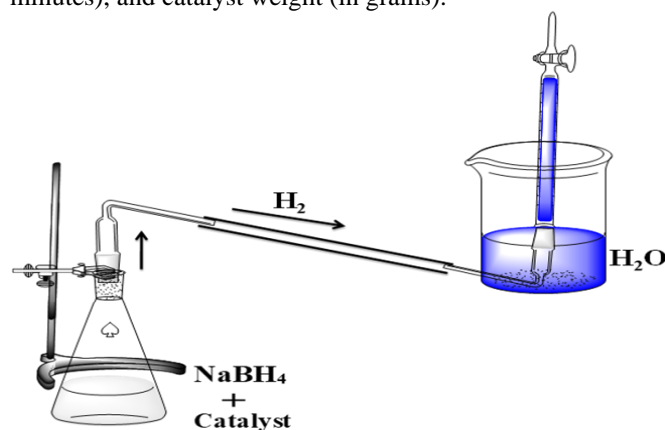
A Phillips 1700 X'Pert (Cu K radiation) records XRD patterns. The TEM-2100 (JEOL, Japan) was used to capture the picture for TEM. A Nicolet spectrophotometer (model 6700) was used to produce FT-IR spectra.

### 2.4. Hydrogen generation from NaBH<sub>4</sub>

The catalytic performance of Cu-BTC was assessed with varied NaBH<sub>4</sub> loadings (0.2, 0.5, 1, 2, and 3 wt/wt.) and Cu-BTC loadings (1, 5, 10, 20, and 50 mg) at 25°C. Using the water displacement method (Fig. 1), the volume of the hydrogen gas emitted was calculated in a 250-mL Erlenmeyer conical flask with a laboratory rubber stopper and a plastic tube connected to a scaled inverted burette (50 mL) filled with water was typically used. The amount of drained water through the inverted burette determines the volume of the released H<sub>2</sub> gas (Fig. 1). The catalyst was typically added to 100 mL of distilled water, followed (by 0.2, 0.5, 1, 2, and 3 wt/wt.) NaBH<sub>4</sub> while being stirred continuously (1000 rpm). Based on the amount of water that was displaced, the total volume of hydrogen was estimated for each period. The total volume of the gas produced represents the production of hydrogen. The reaction temperature (30 °C, 40 °C, and 50 °C) was adjusted via a water bath using 50 mg of Cu-BTC and 1 g of NaBH<sub>4</sub>. The hydrogen generation rates (HGRs, mL min<sup>-1</sup> g<sup>-1</sup>) were calculated using Equation 1 [6]:

$$\text{Hydrogen generation rate (HGR, mL min}^{-1} \text{ g}^{-1}) = \frac{V(\text{mL})}{t(\text{min}) \times \text{Wt. cat}(\text{g})} \quad \text{Eq. 1}$$

Where the water displacement volume (in milliliters), time (in minutes), and catalyst weight (in grams).



**Figure 1.** Water displacement apparatus.

The thermodynamic parameters for the hydrolysis reaction catalyzed by Cu-BTC are calculated using the Arrhenius (Eq. (2)) and Eyring equations (Eq. (3)). [6]

$$\text{Lnk} = -\frac{E_a}{R} \left(\frac{1}{T}\right) + \text{Ln A} \quad \text{Eq. 2}$$

In this equation, k stands for the rate constant, A for the constant, E<sub>a</sub> for the activation energy, R for the gas constant, and T for temperature (K).

$$\text{ln} \left(\frac{k}{T}\right) = \text{ln} \left(\frac{k_B}{h}\right) + \frac{-\Delta H^*}{RT} + \frac{\Delta S^*}{R} \quad \text{Eq. 3}$$

Where k, A, E<sub>a</sub>, R, T, k<sub>B</sub>, h, ΔH\*, and ΔS\* represent the rate constant, a constant, the activation energy (kJ/mol), the gas constant, the absolute temperature in kelvin (K), the Boltzmann constant, the Plank constant, the enthalpy of activation, and the entropy of activation, respectively. Gibbs free energy (ΔG\*) can be calculated using Eq. (4):

$$\Delta G^* = \Delta H^* - T \Delta S^* \quad \text{Eq. 4}$$

The material recyclability was measured for four cycles using 1 mg of Cu-BTC as the catalyst and 3 g of NaBH<sub>4</sub> at 25°C for each cycle. After each cycle, 3 g of NaBH<sub>4</sub> was added to the reaction mixture. The process was monitored as described earlier.

### 3. Results and Discussion

#### 3.1. Catalyst Characterization

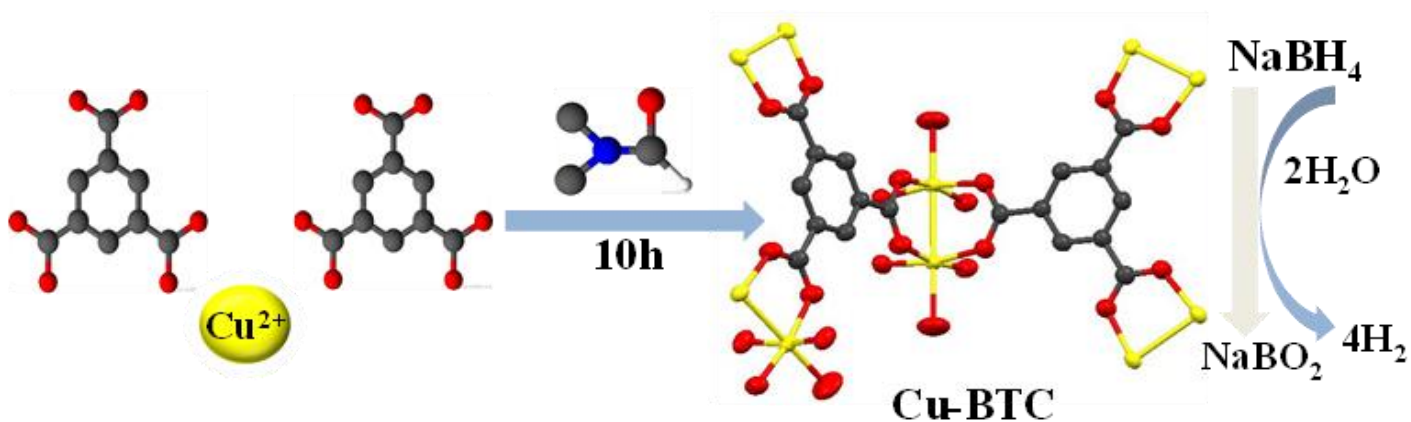
Cu-BTC has a porous crystalline structure comprised of benzene-1,3,5-tricarboxylate and copper ions in a coordinated system of ligands. The copper ions form paddlewheel-like structures connected by the organic ligands, creating a three-dimensional network with large open channels and pores.

Through a hydrothermal process involving BTC and Cu<sup>2+</sup> ions, Cu-BTC MOF is synthesized (Fig. 2). XRD (Fig. 3a), FT-IR (Fig. 3b), and TEM images (Fig. 4) characterize the material. The XRD pattern obtained from the synthesized Cu-BTC crystals provides strong evidence that a pure phase of Cu-BTC has been formed. The distinct diffraction peaks, their specific positions, and intensities confirm that the Cu-BTC crystals have the desired crystal structure, which matches the simulated crystal structure (CCDC-846573, Fig. 3a). This suggests that the synthesized Cu-BTC crystals possess the intended crystal structure, validating the success of the synthesis process. The FTIR analysis (Fig 3b) of the linker and Cu-BTC reveals significant changes during Cu-BTC formation. In Cu-BTC, the characteristic vibrational bands of carboxylic acid groups (-COOH) and aromatic -CH bonds (3073–2554) cm<sup>-1</sup> of the linker disappear, indicating a chemical transformation or coordination with copper ions. Two new bands appear at 1635 cm<sup>-1</sup> and 1368 cm<sup>-1</sup>, corresponding to the asymmetric and symmetric stretch modes of -COO- groups, respectively. These bands suggest proton loss from carboxylic acid and coordination with copper ions. The appearance of a peak at 484 cm<sup>-1</sup> confirms the Cu-O bond [39], providing further evidence for successful Cu-BTC formation. Overall, the FTIR analysis provides compelling evidence of the transformation, involving carboxylic

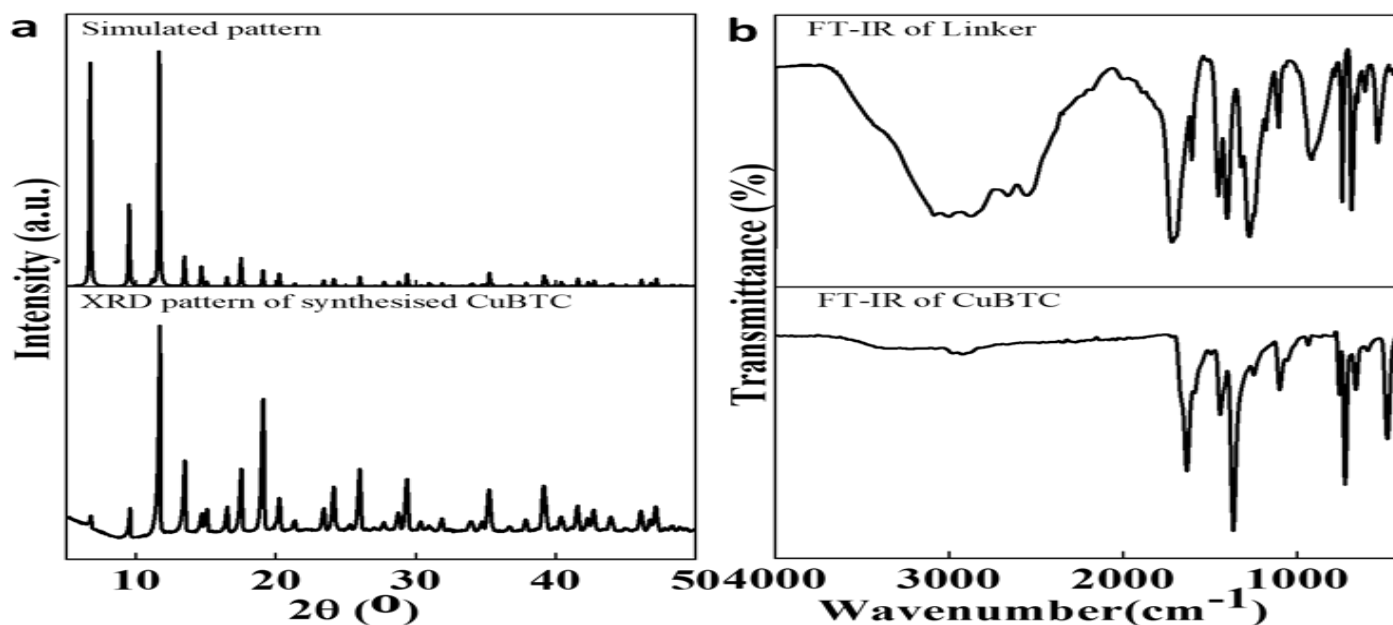
acid proton loss, carboxylate group formation, and copper ion coordination, leading to the formation of Cu-BTC. Cu-BTC crystals are examined using TEM (Fig. 4). They appear as regular, polyhedral structures with sharp edges and vertices. These polyhedral shapes often resemble cubes or truncated cubes, giving rise to the term "cubic morphology." The cubic morphology suggests that the crystal structure of Cu-BTC possesses a high degree of symmetry and order, with well-defined crystal faces.

#### 3.2. Hydrogen generation using Cu-BTC

The evaluation of hydrogen production using various concentrations of NaBH<sub>4</sub> is depicted in Fig. 5. The data analysis reveals that the volume of hydrogen gas increases gradually over time. For various NaBH<sub>4</sub> concentrations (0.2, 0.5, 1, 2, and 3 wt/wt.), the required reaction time to achieve the maximum volume of hydrogen gas decreased to 27 minutes (Fig. 5). This finding suggests that higher concentrations of both the catalyst (Cu-BTC) and NaBH<sub>4</sub> lead to a shorter reaction time (Fig. 5a). The increase in catalyst loading and NaBH<sub>4</sub> concentration facilitates a faster hydrogen generation reaction, resulting in more rapid production of hydrogen gas (Fig. 5a). As the reaction proceeds, the NaBH<sub>4</sub> reactant is gradually consumed, resulting in a decrease in the rate of hydrogen production. This decline can be attributed to the decreasing availability of NaBH<sub>4</sub>, which serves as the source of hydrogen. The reaction rate slows down due to NaBH<sub>4</sub> consumption leading to a decrease in the rate of hydrogen gas production. Fig. 5b illustrates the highest measured HGR of 4386 mL<sub>H<sub>2</sub></sub> g<sub>cat</sub><sup>-1</sup> min<sup>-1</sup>. This value represents the maximum rate at which hydrogen gas is produced per gram of catalyst (Cu-BTC) per minute. A high HGR value indicates a fast and efficient hydrogen generation process, demonstrating the effectiveness of Cu-BTC as a catalyst for hydrogen production from NaBH<sub>4</sub>. Remarkable results were achieved in the hydrogen production process using a simple approach at room temperature and without adjusting the pH.

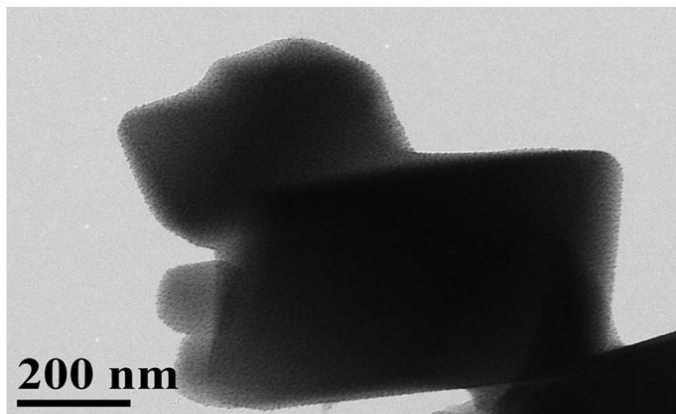


**Figure 2.** Cu-BTC synthesis and its applications via NaBH<sub>4</sub> hydrolysis.



**Figure 3.** Characterization of Cu-BTC using a) XRD and b) FT-IR.

To assess the recyclability of the catalysts, further investigations were conducted (Fig. 5c-d). The results show that Cu-BTC can be utilized in consecutive cycles without significant loss of the material's catalytic performance for the four runs. The findings show that the material is very recyclable. This suggests that Cu-BTC is structurally stable and does not undergo substantial degradation or structural changes that would hinder its performance. The recyclability of Cu-BTC implies that it can be utilized repeatedly, potentially in numerous catalytic reactions or processes, before it needs to be replaced. Additionally, it reduces waste generation associated with catalyst disposal, contributing to environmental sustainability.



**Figure 4.** TEM image of Cu-BTC.

This observation indicates that Cu-BTC is a potentially valuable catalyst for various industrial applications, providing economic and environmental benefits through its recyclable nature. The impact of reaction temperature (30–50 °C) on hydrolysis-based hydrogen generation for Cu-BTC was examined (Fig. 6). As the reaction temperature rises, the rate of hydrogen production also rises (Fig. 6). This is due to the increase in the

kinetic of the hydrolysis of  $\text{NaBH}_4$ . This increased kinetic energy results in more energetic collisions between the hydrogen molecules and the active sites on the Cu-BTC catalyst. These collisions facilitate faster and more efficient reactions, leading to higher HGRs values. The Arrhenius equation is employed to determine the activation energy for the hydrolysis of  $\text{NaBH}_4$  using Cu-BTC (Eq. 2). According to the thermal calculation, Cu-BTC has an activation energy of  $41.7 \text{ kJ mol}^{-1}$  (Fig. 7a). This value provides important information about the energy barrier associated with the reaction. This lower activation energy implies that the reaction can proceed more easily at lower temperatures. Table 1 displays the thermodynamic parameters computed for the hydrolysis reaction when Cu-BTC acts as a catalyst. These calculations are based on the application of both the Arrhenius equation (Eq. (2)) and the Eyring equation (Eq. (3)). Additionally, Fig. 7a-b graphically represents the results obtained.

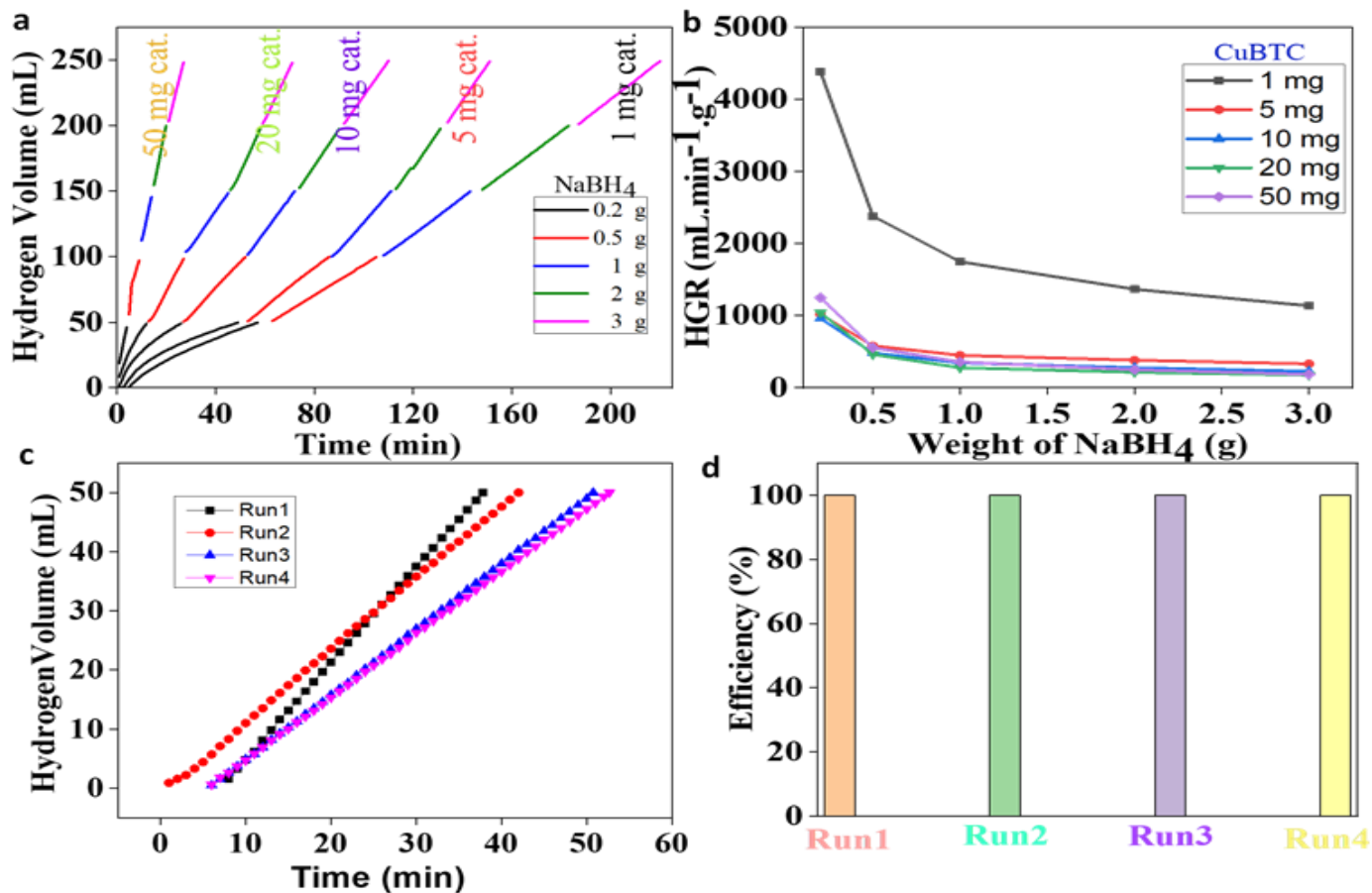
**Table 1:** Thermodynamic parameters for catalytic hydrolysis of  $\text{NaBH}_4$  using Cu-BTC. Reaction condition: 1mg. catalyst; 3g  $\text{NaBH}_4$ .

T (K)	$E_a$ (kJ/mol)	$\Delta H^*$ (kJ/mol)	$\Delta S^*$ (kJ/mol)	$\Delta G^*$ (kJ/mol·K)
303	41.7	39.11	0.14	-3.31
313				-4.71
323				-6.11

In an aqueous solution,  $\text{NaBH}_4$  dissociates into  $\text{BH}_4^-$  and  $\text{Na}^+$  ions [46]. These ions then diffuse and become adsorbed onto the surface of the Cu-BTC. The  $\text{BH}_4^-$  ions, and water ( $\text{H}_2\text{O}$ ) react on the active sites of the Cu-BTC surface to produce hydrogen gas ( $\text{H}_2$ ). The hydrogen gas subsequently desorbs from the Cu-BTC. As a result of these reactions, four molecules of hydrogen gas are liberated, while  $\text{NaBO}_2$  and additional water molecules are formed as byproducts. This reaction is depicted in Fig. 2.

**Table 2** summarizes several catalysts that can be utilized to produce hydrogen via NaBH<sub>4</sub> hydrolysis, including Ref. [40-41]. Comparing this study's hydrolysis conditions to those of several reported catalysts, they are fairly straightforward the comparison reveals some significant advantages of Cu-BTC. Cu-BTC stands out because it does not require the addition of a basic solution, such as NaOH, which is reported for catalysts like NiB/NiFe<sub>2</sub>O<sub>4</sub> [40], CoB@ZIF-8 [41], zeolitic imidazolate framework-9 (ZIF-9) [42], and Zn1Co1-Co@NC [43]. The absence of a basic solution simplifies the hydrolysis process and makes it more straightforward. Another advantage of Cu-BTC is the minimal loading required. The study reports that the hydrolysis reaction can be accomplished with just 1 mg of Cu-

BTC at room temperature. In contrast, other catalysts may require higher loadings or contain multiple types of metals, which can complicate the catalyst synthesis and increase costs. Furthermore, Cu-BTC contains one type of metal, which is copper. This is in contrast to other catalysts that involve multiple types of metals [40][43]. The use of a single metal simplifies the catalyst composition and potentially enhances its stability and activity. Overall, the study suggests that Cu-BTC exhibits superior catalytic performance compared to several reported catalysts for the hydrolysis of NaBH<sub>4</sub>. It implies that Cu-BTC demonstrates better hydrogen production efficiency, reaction kinetics, or other desirable characteristics.



**Figure 5.** Hydrogen generation from (a) NaBH<sub>4</sub> hydrolysis, (b) hydrogen generation rate, and c-d) recyclability of Cu-BTC.

**Table 2:** Comparison via catalysts used for hydrolysis of NaBH<sub>4</sub>.

Catalysts	Reaction Conditions	HGR (mL <sub>H2</sub> ·g <sub>cat</sub> <sup>-1</sup> ·min <sup>-1</sup> )	Ref.
NiB/NiFe <sub>2</sub> O <sub>4</sub>	Cat. 100 mg; NaBH <sub>4</sub> (5 wt.%); NaOH (5 wt.%), 25 °C	300	[40]
WSC -Ni	Cat. 100 mg; NaBH <sub>4</sub> (1.0 g/L), 30 °C	130	[44]
ZIF-9	Cat. 25mg; NaBH <sub>4</sub> (5 wt.%); NaOH (5 wt.%), 40 °C	3642	[42]
Zn1Co1-Co@NC	Cat. 10 mg; NaBH <sub>4</sub> (100 mg); NaOH (0.8 g), 30 °C	1807	[43]
CoB@ZIF-8	Cat. 10 mg; NaBH <sub>4</sub> (1.67 wt. %); NaOH (5 wt.%), 30 °C	453.6	[41]
Fe <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub> -Fe	Cat. 50 mg; NaBH <sub>4</sub> (5.28 M), 100 °C	1057	[45]
Cu-BTC	Cat. 1 mg; NaBH <sub>4</sub> (2-3 wt. %), 25 °C	4386	This study

**Notes:** WSC, Wheat straw cellulose; Zeolitic imidazolate frameworks-9, ZIF-9

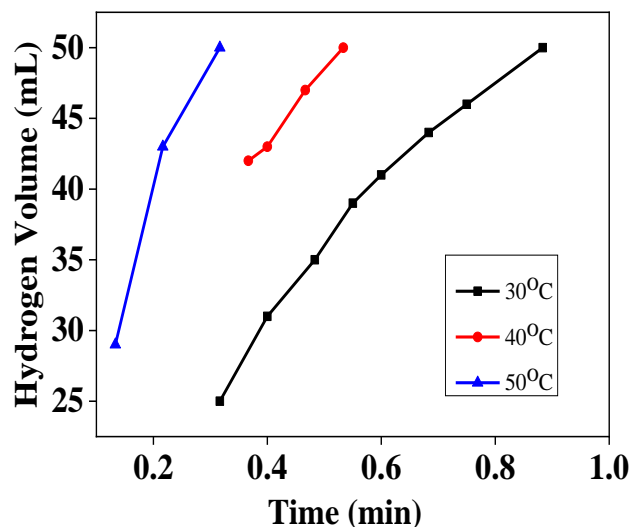


Figure 6. Hydrogen generation from NaBH<sub>4</sub>.

## 4. Conclusion

Cu-BTC has been successfully synthesized, characterized, and utilized as a successful catalyst for the production of environmentally-friendly hydrogen gas from the hydrolysis of NaBH<sub>4</sub>. Cu-BTC achieves impressive maximum HGRs of 4386 mL<sub>H<sub>2</sub></sub> g<sub>cat</sub><sup>-1</sup> min<sup>-1</sup> using low catalyst loading (1 mg) with a low activation energy of 41.7 kJ mol<sup>-1</sup>. Cu-BTC's catalytic performance in hydrogen generation is outstanding, characterized by its high efficiency, rapid reaction time, and minimal catalyst usage. Moreover, the material's recyclability was investigated, revealing that it can maintain hydrogen production for up to four cycles without a noticeable decline in performance. These findings emphasize Cu-BTC's potential as a valuable catalyst for sustainable hydrogen production.

## Acknowledgments

The Science, Technology, and Innovation Funding Authority (Project No. 44686) has provided support for this project.

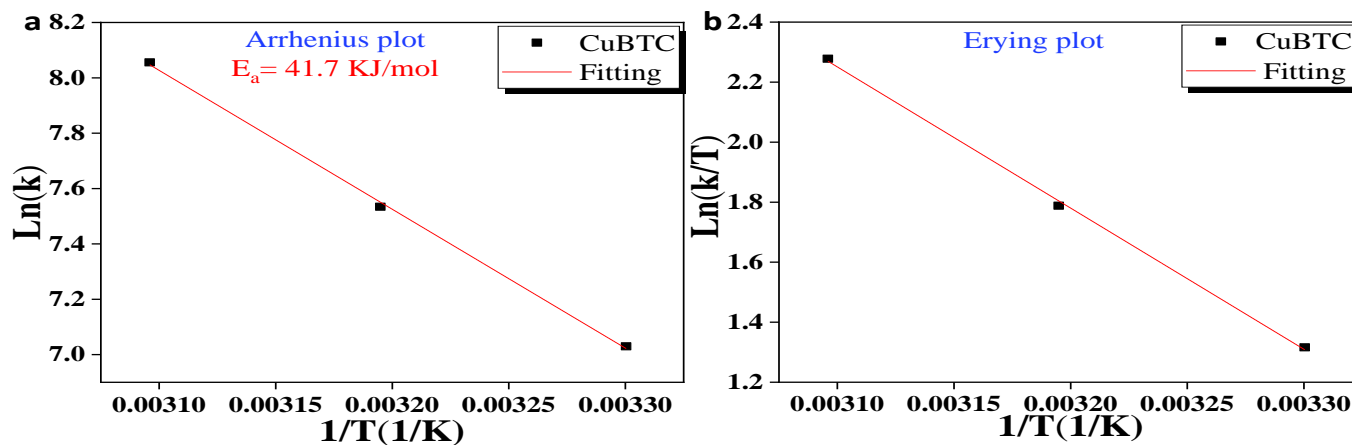


Figure 7. (a) Arrhenius plot between Ln (k) versus 1/T. and (b) Eyring plot between Ln (k/T) versus 1/T.

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