Cu$_{0.4}$Co$_{0.6}$MoO$_4$ Nanorods Supported on Graphitic Carbon Nitride as a Highly Active Catalyst for the Hydrolytic Dehydrogenation of Ammonia Borane

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Abstract: As a typical chemical hydride, ammonia borane (AB) has received extensive attention because of its safety and high hydrogen storage capacity. The aim of this work was to develop a cost-effective and highly reactive catalyst for hydrolyzing AB. Herein, we synthesized a series of Cu$_x$Co$_{1-x}$MoO$_4$ dispersed on graphitic carbon nitride (g-C$_3$N$_4$) to dehydrogenate AB. Among those Cu$_x$Co$_{1-x}$MoO$_4$/g-C$_3$N$_4$ catalysts, Cu$_{0.4}$Co$_{0.6}$MoO$_4$/g-C$_3$N$_4$ exhibited the highest site time yield (STY) value of 75.7 mol H$_2$ mol$_{cat}^{-1}$ min$^{-1}$ with a low activation energy of 14.46 kJ mol$^{-1}$. The STY value for Cu$_{0.4}$Co$_{0.6}$MoO$_4$/g-C$_3$N$_4$ was about 4.3 times as high as that for the unsupported Cu$_{0.4}$Co$_{0.6}$MoO$_4$, indicating that the g-C$_3$N$_4$ support plays a crucial role in improving the catalytic activity. Considering its low cost and high catalytic activity, our Cu$_{0.4}$Co$_{0.6}$MoO$_4$/g-C$_3$N$_4$ catalyst is a strong candidate for AB hydrolysis for hydrogen production in practical applications.

Keywords: hydrogen production; ammonia borane; graphitic carbon nitride; nanorods

1. Introduction

With the rapid development of social economy and technology, the consumption of fossil fuels keeps growing, leading to the destruction of the environment and ecology [1,2]. Hydrogen energy, generating H$_2$O after reaction, can effectively solve the contradiction in the current energy structure between developing need and the environment [3]. To realize the vision of hydrogen power popularization, problems of hydrogen storage and acquisition must be overcome [4]. Chemical hydrogen storage, one of the most popular approaches, is the process by which hydrogen is trapped in a liquid or solid and can be extracted in due course. Ammonia borane (AB), with its high hydrogen density (19.6%), low molar molecular weight (30.7 g mol$^{-1}$), and high stability, is a high-profile hydrogen storage material [5–8]. When appropriate catalysts are used, the activation energy of the reaction is reduced, and the AB produces a large amount of hydrogen under mild conditions according to the following reaction [9,10]:

$$\text{NH}_3\text{BH}_3 + 2\text{H}_2\text{O} \rightarrow \text{NH}_4\text{BO}_2 + 3\text{H}_2$$

In the literature, great efforts have been made to develop noble-metal-based catalysts [11]. However, their large-scale applications are remarkably limited by their high costs. Although the costs of bimetallic catalysts composed of both noble and nonnoble metals, such as Au–Ni, Ru–Ni, etc., are reduced in contrast to those of the noble metal catalysts, they are still high [12,13]. Thus, it is important for us to further reduce the cost of catalysts by developing noble-metal-free catalysts. On the
other hand, the introduction of supports is one of the most efficient strategies for restraining the agglomeration of nanoparticles during a catalytic reaction. Due to its unique structure, inexpensiveness, and high specific surface area, carbon nitride (g-C$_3$N$_4$) has proved to be an ideal support in the field of heterogeneous catalysis, such as in photocatalysis, electrocatalysis, and the oxidation of toluene [14–16]. In recent years, there have been several successful examples of the application of g-C$_3$N$_4$ as a catalyst support in AB dehydrogenation. For example, Guo et al. designed g-C$_3$N$_4$-supported Au–Co nanoparticles with a site yield (STY) value of 28.4 mol$_{H_2}$mol$_{cat}^{-1}$ min$^{-1}$ [17]. In contrast, the STY value for the resultant catalysts was 969 mol$_{H_2}$mol$_{cat}^{-1}$ min$^{-1}$ [18]. Hamza et al. reported that the STY value of AgPd/g-C$_3$N$_4$ was 94.1 mol$_{H_2}$mol$_{cat}^{-1}$ min$^{-1}$ [19]. Jia et al. synthesized Pb(0) nanoparticles anchored into g-C$_3$N$_4$ with chitosan, and their STY value was 27.7 mol$_{H_2}$mol$_{cat}^{-1}$ min$^{-1}$ at 30 °C [20]. Fan et al. synthesized AgCo bimetallic nanoparticles supported on g-C$_3$N$_4$, and the STY value of Ag$_{0.1}$Co$_{0.9}$/g-C$_3$N$_4$ was 249.02 mol$_{H_2}$mol$_{cat}^{-1}$ min$^{-1}$ [21]. It should be noted that the applications of g-C$_3$N$_4$ as a support in AB dehydrogenation are still rarely reported. In addition, the active components were noble metal or noble-metal-containing alloys in those reports. Therefore, it is important to explore some other types of active components supported on g-C$_3$N$_4$ and investigate their activity in AB dehydrogenation.

Herein, we report a series of Cu$_x$Co$_{1−x}$/MoO$_4$ supported on g-C$_3$N$_4$ for ammonia borane hydrolysis. As far as we know, a noble-metal-free catalyst supported on g-C$_3$N$_4$ towards AB hydrolysis has not been reported previously. In this work, we found that the catalytic activity of the catalysts was closely related with the molar ratio of Co to Cu in Cu$_x$Co$_{1−x}$/MoO$_4$/g-C$_3$N$_4$. It was discovered that Cu$_{0.5}$Co$_{0.5}$/MoO$_4$/g-C$_3$N$_4$ shows the best catalytic activity as its STY value can reach 75.7 mol$_{H_2}$mol$_{cat}^{-1}$ min$^{-1}$, which is better than the properties of most non-precious metals reported in the literature. In addition, Cu$_{0.4}$Co$_{0.6}$/MoO$_4$/g-C$_3$N$_4$ exhibited higher catalytic activity in contrast to the unsupported counterpart, Cu$_{0.4}$/Co$_{0.6}$/MoO$_4$.

2. Results and Discussion

Figure 1 shows the Powder X-ray diffraction (XRD) patterns of g-C$_3$N$_4$ before loading and Cu$_{0.4}$Co$_{0.6}$/MoO$_4$/g-C$_3$N$_4$. Evidently, the peaks of g-C$_3$N$_4$, CuMoO$_4$, and CoMoO$_4$ can be found in Cu$_{0.4}$Co$_{0.6}$/MoO$_4$/g-C$_3$N$_4$. The diffraction peak at 27.7° can be observed in both XRD patterns and is the characteristic peak of g-C$_3$N$_4$. The diffraction peaks of Cu$_{0.4}$Co$_{0.6}$/MoO$_4$/g-C$_3$N$_4$ at 23.4°, 36.5°, 38.6°, 43.1°, and 52.9° correspond to the (110), (002), (200), (112), and (130) planes of CuMoO$_4$ (PDF#26-0546). The peaks at 26.5°, 40.2°, and 46.3° correspond to the (002), (003), and (403) planes of CoMoO$_4$ (PDF#21-0868). No other peaks of impurities can be observed in the XRD pattern, indicating that the composites mainly contain C$_3$N$_4$, CoMoO$_4$, and CuMoO$_4$. For comparison, a series of Cu$_x$Co$_{1−x}$/MoO$_4$/g-C$_3$N$_4$ were synthesized, and their XRD patterns are shown in Figure S1.

The Fourier transform infrared (FTIR) spectra of Cu$_{0.4}$Co$_{0.6}$/MoO$_4$, Cu$_{0.4}$/Co$_{0.6}$/MoO$_4$/g-C$_3$N$_4$, and pure g-C$_3$N$_4$ are shown in Figure 2. For pure g-C$_3$N$_4$ powder, the main peaks at 815, 1240, 1316, 1400, 1458, 1573, and 1640 cm$^{-1}$ can be seen, due to the stretching vibration modes of C=N and C=N, which is similar to previous reports [20,22,23]. For Cu$_{0.4}$/Co$_{0.6}$/MoO$_4$/g-C$_3$N$_4$, the bands in the range of 1240–1640 cm$^{-1}$ correspond to the bonds of pure g-C$_3$N$_4$. In contrast, the bands at 937, 615, and 475 cm$^{-1}$ are assigned to the stretching vibrations of the t-MoO$_4$ group, Mo=O stretching, and Mo=O=Mo bending vibrations [24–26]. This result further confirms that Cu$_{0.4}$/Co$_{0.6}$/MoO$_4$ nanorods were successfully loaded onto g-C$_3$N$_4$. The FTIR spectra of different Cu$_x$Co$_{1−x}$/MoO$_4$/g-C$_3$N$_4$ samples are shown in Figure S2 and are similar to that of Cu$_{0.4}$/Co$_{0.6}$/MoO$_4$/g-C$_3$N$_4$. 

The morphology of g-C$_3$N$_4$ into the synthetic system did not change the morphology and size of the Cu result from the Cu composites mainly contain and the results (PDF#21…). Jia et al. synthesized Pb(0) nanoparticles anchor and investigate their activity in AB dehydrogenation. For example, Guo et al. designed…strecthing vibrations of C=N and C=O. As displayed in Figure S3, the relative peak heights of Co to Cu decrease as...

Figure 1. XRD patterns of graphitic carbon nitride (g-C$_3$N$_4$) and Cu$_{0.4}$Co$_{0.6}$MoO$_4$/g-C$_3$N$_4$ (a) and enlarged XRD pattern of Cu$_{0.4}$Co$_{0.6}$MoO$_4$/g-C$_3$N$_4$ (b).

Figure 2. FTIR spectra of Cu$_{0.4}$Co$_{0.6}$MoO$_4$, g-C$_3$N$_4$, and Cu$_{0.4}$Co$_{0.6}$MoO$_4$/g-C$_3$N$_4$.

The field-emission scanning electron microscope (FESEM) images and Energy Dispersive Spectrometer (EDS) spectra of the catalysts are shown in Figure 3 and Figure S3, respectively. The morphology of g-C$_3$N$_4$ in Figure 3a is similar to that in a previous report [6]. The unsupported Cu$_{0.4}$Co$_{0.6}$MoO$_4$ is shown in Figure 3b,c, which shows aggregated nanorods with a diameter of ca. 500 nm. We note that most of the rods agglomerate together and form large aggregates, leading to a reduction in the contact area of the catalyst and substrate in the catalysis. To disperse Cu$_{0.4}$Co$_{0.6}$MoO$_4$ well and increase the number of exposed active sites, we introduced g-C$_3$N$_4$ into solution during the synthesis process and successfully obtained the Cu$_{0.4}$Co$_{0.6}$MoO$_4$/g-C$_3$N$_4$ material (Figure 3d,e). The rods could be easily found on the surface of g-C$_3$N$_4$. The diameter of the rods was still ca. 500 nm, and the length was ca. 5–10 μm. This observation indicates that the introduction of the g-C$_3$N$_4$ into the synthetic system did not change the morphology and size of the Cu$_{0.4}$Co$_{0.6}$MoO$_4$ nanorods. However, their dispersion was remarkably improved. EDS analysis was carried out on the nanorods, and the results are shown in Figure 3f. The elements C, N, O, Mo, Co, and Cu were detected. Evidently, the elements C and N come from the g-C$_3$N$_4$ material, while the elements O, Mo, Co, and Cu result from the Cu$_{0.4}$Co$_{0.6}$MoO$_4$. As displayed in Figure S3, the relative peak heights of Co to Cu decrease as x increases. The molar ratios of the different elements are shown in Table S1, indicating that the actual ratios of Co, Cu, and Mo in Cu$_x$Co$_{1-x}$MoO$_4$/g-C$_3$N$_4$ are close to the theoretical values.
The valence states of the elements in Cu$_{0.4}$Co$_{0.6}$MoO$_4$/$g$-C$_3$N$_4$ were measured by X-ray photoelectron spectrometer (XPS), and the results are shown in Figure 4. The peaks at 284.4 eV and 287.7 eV correspond to C 1s, assigned to carbon atoms on the surface and coordination between carbon atoms and nitrogen atoms, respectively [23]. The N 1s spectrum separated into two peaks at 398.4 eV and 400.1 eV, which were assigned to sp$^2$-hybridized nitrogen in triazine rings (C–N=C) and tertiary nitrogen (N–(C)$_3$) groups [27]. The Co 2p spectrum shows two peaks at 780.9 eV and 796.1 eV of the Co 2p$_{3/2}$ and Co 2p$_{1/2}$ energy levels, demonstrating that Co is divalent [28]. At the same time, the peaks of Cu 2p at 931.8 eV and 951.7 eV imply the existence of Cu$^{2+}$. Figure 4e is the XPS spectrum of Mo 3d. Two peaks at 232.2 eV and 235.3 eV imply that the element Mo is present as Mo$^{6+}$ [29]. The peak at 531.3 eV in the O 1s spectrum illustrates the existence of O$^{2−}$ [30]. Considering the XRD, SEM, and XPS results together, we can conclude that our obtained product is $g$-C$_3$N$_4$-supported Cu$_{0.4}$Co$_{0.6}$MoO$_4$.

The catalytic activity levels of $g$-C$_3$N$_4$, Cu$_{0.4}$Co$_{0.6}$MoO$_4$, and Cu$_{0.4}$Co$_{0.6}$MoO$_4$/$g$-C$_3$N$_4$ in the hydrolysis of ammonia borane were tested at 293 K. It can be seen in Figure 5 that $g$-C$_3$N$_4$ had no catalytic activity in the hydrolytic reaction. In addition, the catalytic activity of unsupported Cu$_{0.4}$Co$_{0.6}$MoO$_4$ was significantly lower than that of Cu$_{0.4}$Co$_{0.6}$MoO$_4$/$g$-C$_3$N$_4$. The STY values were 75.7 mol$_{H_2}$ mol$_{cat}^{-1}$ min$^{-1}$ for Cu$_{0.4}$Co$_{0.6}$MoO$_4$/$g$-C$_3$N$_4$ and 17.6 mol$_{H_2}$ mol$_{cat}^{-1}$ min$^{-1}$ for the unsupported Cu$_{0.4}$Co$_{0.6}$MoO$_4$. As discussed above, the introduction of $g$-C$_3$N$_4$ into the catalysts can help to disperse active materials and thereby improve the catalytic property tremendously. Notably, the molar ratio of hydrogen to ammonia borane reached 3, demonstrating that complete hydrogen release can be achieved when Cu$_{0.4}$Co$_{0.6}$MoO$_4$/$g$-C$_3$N$_4$ acts as a catalyst. Figure 6 illustrates catalytic hydrolysis on the unsupported Cu$_{0.4}$Co$_{0.6}$MoO$_4$ and Cu$_{0.4}$Co$_{0.6}$MoO$_4$/$g$-C$_3$N$_4$ clearly. We also tried to synthesize ZnMoO$_4$ by a similar strategy to measure the catalysis activity of other molybdates. The result that there was no catalysis activity in ZnMoO$_4$ illustrates that molybdates have no reactivity. However, according to the literature, molybdates can serve as a Lewis acid and conduct the adsorption of OH$^-$ on the catalyst surface, which would be of benefit to the hydrolysis reaction [31].
which is lower than those of Cu/MoO₄ within the first min. After then, hydrogen constantly produced. This observation indicates that the introduction of g-C₃N₄ enhanced the catalytic activity. In contrast, all the Cu/MoO₄ systems no hydrogen release, indicating that molybdates have no reactivity. However, Co/MoO₄ and Cu/MoO₄/g-C₃N₄, further confirming that the introduction of g-C₃N₄ enhanced the catalytic activity. We also synthesized CoMoO₄/g-C₃N₄, further confirming that the introduction of g-C₃N₄ enhanced the catalytic activity. In addition, the catalytic activity of unsupported Cu/MoO₄ has significantly lower than that of Cu/MoO₄/g-C₃N₄, indicating that the introduction of g-C₃N₄ enhanced the catalytic activity. The best molar ratio of Cu to Co and Cu/MoO₄ was 1:1 (H₂/N(AB), indicating that Cu/MoO₄ as a catalyst, there is no induction period in AB. We also synthesized CoMoO₄/g-C₃N₄ and CuMoO₄/g-C₃N₄, further confirming that the introduction of g-C₃N₄ enhanced the catalytic activity.

**Figure 4.** XPS pattern of Cu₀.₄Co₀.₆MoO₄/g-C₃N₄: (a) C 1s; (b) N 1s; (c) Cu 2p; (d) Co 2p; (e) Mo 3d; (f) O 1s.

**Figure 5.** Time vs. n(H₂)/n(AB) during the catalytic hydrolysis of ammonia borane (AB) with catalysts Cu₀.₄Co₀.₆MoO₄, g-C₃N₄ and Cu₀.₄Co₀.₆MoO₄/g-C₃N₄.
In consideration of variation of the molar ratio of cobalt to copper, we synthesized a series of 
Cu$_x$Co$_{1-x}$MoO$_4$/g-C$_3$N$_4$ ($x = 0, 0.2, 0.4, 0.6, 0.8, 1$) samples to test their catalytic performance, shown in Figure 7. No matter the value of $x$, Cu$_{0.2}$Co$_{0.8}$MoO$_4$/g-C$_3$N$_4$ samples were active in the hydrolysis of ammonia borane. CuMoO$_4$/g-C$_3$N$_4$, without Co element, showed the lowest catalytic activity with a STY value of 11.7 mol H$_2$/mol cat$^{-1}$ min$^{-1}$. When Co element was present, the activities increased remarkably, and the best molar ratio of Cu to Co was 4:6 with a STY value of 75.7 mol H$_2$/mol cat$^{-1}$ min$^{-1}$. It is worth noting that the STY of CoMoO$_4$/g-C$_3$N$_4$ was 35.35 mol H$_2$/mol cat$^{-1}$ min$^{-1}$, which is lower than those of Cu$_{0.2}$Co$_{0.8}$MoO$_4$/g-C$_3$N$_4$, Cu$_{0.4}$Co$_{0.6}$MoO$_4$/g-C$_3$N$_4$, and Cu$_{0.6}$Co$_{0.4}$MoO$_4$/g-C$_3$N$_4$, indicating that the coexistence of cobalt and copper in the sample is helpful to improving the catalytic activity. Notably, when CoMoO$_4$ served as a catalyst, there was no hydrogen released from the AB solution within the first minute. After then, hydrogen was constantly produced. This observation indicates that there is an induction period for the CoMoO$_4$ catalyst. In contrast, all the Cu-containing catalysts in this study had no induction period in AB hydrolysis, illustrating that copper element can shorten the induction period of catalysis. These conclusions are in a good agreement with those in previous reports [22,32]. We also synthesized CoMoO$_4$ and CuMoO$_4$, which had STY values of 25.5 and 3.9 mol H$_2$/mol cat$^{-1}$ min$^{-1}$, respectively; these STY values are lower than those of CoMoO$_4$/g-C$_3$N$_4$ and CuMoO$_4$/g-C$_3$N$_4$, further confirming that the introduction of g-C$_3$N$_4$ enhanced the catalytic activity.

To understand the relationship between catalyst dosage and hydrogen production rate, the hydrogen evolution curves for different amounts of Cu$_{0.4}$Co$_{0.6}$MoO$_4$/g-C$_3$N$_4$ are shown in Figure 8. As the amount of Cu$_{0.4}$Co$_{0.6}$MoO$_4$/g-C$_3$N$_4$ increased, the rate of hydrogen production also increased. By fitting the curve of ln(catalyst) vs. ln(rate), the relationship between the catalyst dosage and the hydrogen production rate was clarified. As shown in Figure 8b, the slope of the fitted curve was 0.901, indicating that the hydrolytic process is a pseudo-first-order reaction in the initial stage.

![Figure 6](image_url)  
**Figure 6.** Scheme of the catalytic properties of bulk Cu$_{0.4}$Co$_{0.6}$MoO$_4$ and Cu$_{0.4}$Co$_{0.6}$MoO$_4$/g-C$_3$N$_4$.  

- **n(H$_2$)/n(AB)** during the catalytic hydrolysis of AB with catalyst Cu$_x$Co$_{1-x}$MoO$_4$/g-C$_3$N$_4$:  
  - (a) Time vs. $n(H_2)/n(AB)$  
  - (b) STY values with $x$ for Cu$_{0.4}$Co$_{0.6}$MoO$_4$/g-C$_3$N$_4$.  

- **NH$_3$BH$_3$**  
  - 75.7  
  - 17.6  

- **CO$_2$**  
- **Mo**  
- **Cu**  
- **H$_2$**  
- **N**  
- **C**  
- **Cu$_{0.4}$Co$_{0.6}$MoO$_4$**  
- **H$_2$**

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stage. The hydrogen production rates of the catalysts decreased gradually due to the diffusion rate limitation of AB and catalyst poisoning. This result is consistent with those in previous literature [5]. Therefore, hydrogen production can be controlled easily by adjusting the catalyst dosage in practice.

Figure 8. (a) \( n(H_2)/n(AB) \) vs. reaction time at different \( Cu_{0.4}Co_{0.6}MoO_4/g-C_3N_4 \) dosages; (b) the relationship between the logarithms of the catalyst mass and the catalytic rate.

Figure 9a shows the relationship between the amount of ammonia borane and the volume of hydrogen production. It is interesting to note that the hydrogen release rates were almost the same at the initial stage of the hydrolytic reaction, demonstrating that the AB concentration has no pronounced effect on the initial reaction rate of hydrogen production. As shown in Figure 9b, the slope of ln(rate) vs. ln(NH\(_3\)BH\(_3\)) was 0.0222, which is close to zero, indicating that the catalytic reaction rate is independent of the AB concentration due to a zero-order reaction.

Figure 9. (a) Volume of hydrogen vs. reaction time at different \( Cu_{0.4}Co_{0.6}MoO_4/g-C_3N_4 \) dosages; (b) the relationship between the logarithms of the catalyst mass and the catalytic rate.

As we know, the temperature exerts a significant influence on catalytic activity of a catalyst. We also explored the relationship between the rate of hydrogen generation and catalytic temperature in the range 298 to 313 K (Figure 10). With increasing temperature, the slope of the hydrogen evolution curve became larger, and the time taken for complete hydrogen release became shorter. According to Arrhenius formula, the apparent activation energy (E\(_a\)) can be calculated after fitting the curve of ln k vs. 1/T, where the k value is the slope of hydrogen generation vs. time. The E\(_a\) value of \( Cu_{0.4}Co_{0.6}MoO_4/g-C_3N_4 \) was as low as 14.46 kJ mol\(^{-1}\). In general, E\(_a\) can be used to roughly assess the catalytic activity of a catalyst. The low activation energy indicates that its energy barrier is low in the catalytic process, hinting that the catalysts possess high catalytic activity. Table 1 lists the STY values and activation energy data of some representative noble-metal-free catalysts in the literature and those of our \( Cu_{0.4}Co_{0.6}MoO_4/g-C_3N_4 \). As can be seen, the STY value of \( Cu_{0.4}Co_{0.6}MoO_4/g-C_3N_4 \) is higher than those of most noble-metal-free catalysts in the literature. Therefore, \( Cu_{0.4}Co_{0.6}MoO_4/g-C_3N_4 \) is one of the best potential catalysts for AB hydrolysis.
was used during the experiment. To synthesize g-C₃N₄ catalysts above, except that no g-C₃N₄ samples were centrifugally separated, washed, dried, and finally calcined at 350°C to adjust the pH of the suspension to 7. Finally, the suspension was transferred into a Teflon-lined reactor. The molar ratios of Cu to Co in the mixture solution was dropped into the g-C₃N₄/graphene 66.7 2.3 / / [37]

C₂O₃/g-C₃N₄ 45 / / 51.9 [38]

Cu₈Ni₉/CH₄ 41.9 / / 40.533 [39]

CuCo/graphene 41 12 / / 54.89 [40]

NiP 40.4 / / 44.6 [5]

NiP/PₐrGO 13.3 / / 34.7 [41]

Ni/g-C₃N₄ 18.7 / / 36 [6]

Table 1. Comparison of the STY value and apparent activation energy of our Cu₉₀₄Co₉₆MoO₄/g-C₃N₄ catalyst with those of some other representative noble-metal-free catalysts in the literature.

3. Materials and Methods

3.1. Synthesis of Catalysts

All chemical reagents were analytically pure and had not been further purified. Deionized water was used during the experiment. To synthesize g-C₃N₄, 25 g urea was calcined at 550°C for 6 hours in air with a heating rate of 2.5°C min⁻¹. A resultant yellow soft and porous powder was obtained. For the purpose of synthesizing 10 wt % Cu₉₀₄Co₉₆MoO₄/g-C₃N₄, 0.4 g g-C₃N₄ was dispersed in 40 mL ethanol and 20 mL deionized water. Then, 0.18 mmol copper chloride and cobalt chloride mixture solution was dropped into the g-C₃N₄ suspension under magnetic stirring for 2 hours. After that, 0.18 mmol sodium molybdate was added into the mixture solution. The molar ratios of Cu to Co to Mo were set at x:(1–x):1 (x = 0, 0.2, 0.4, 0.6, 0.8, 1). Then, 0.1 M ammonium hydroxide was used to adjust the pH of the suspension to 7. Finally, the suspension was transferred into a Teflon-lined stainless reaction vessel, which was placed in an oven and heated at 160°C for 8 hours. The obtained samples were centrifugally separated, washed, dried, and finally calcined at 350°C for 2 hours. For comparison, unsupported Cu₉₀₄Co₉₆MoO₄ was also prepared in a similar process to that described above, except that no g-C₃N₄ was used.

3.2. Characterizations

Powder X-ray diffraction (XRD) was measured to obtain crystallographic information using a Bruker D8 Discover X-ray diffractometer with Cu Kα radiation (λ = 1.5406Å) in the range of
were tested at 298 K. Typically, 5.0 mg of active substance was dispersed in 5 mL deionized water. Then, 15 mL of mixture solution of 3 mmol ammonia borane and 20 mmol NaOH was quickly added to the Cu$_x$Co$_{1-x}$MoO$_4$/g-C$_3$N$_4$ solution. The volume of the generated hydrogen was measured by a drainage method, and the hydrogen production was recorded at intervals.

3.3. Catalytic Experiments

Due to the significant influence of temperature on catalytic performance, the catalyst properties were tested at 298 K. Typically, 5.0 mg of active substance was dispersed in 5 mL deionized water. Then, 15 mL of mixture solution of 3 mmol ammonia borane and 20 mmol NaOH was quickly added to the Cu$_x$Co$_{1-x}$MoO$_4$/g-C$_3$N$_4$ solution. The volume of the generated hydrogen was measured by a drainage method, and the hydrogen production was recorded at intervals.

4. Conclusions

In summary, we synthesized a series of Cu$_x$Co$_{1-x}$MoO$_4$/g-C$_3$N$_4$ ($x = 0, 0.2, 0.4, 0.6, 0.8, 1$) and unsupported Cu$_{0.4}$Co$_{0.6}$MoO$_4$ for the hydrolysis of ammonia borane. As a representative catalyst, Cu$_{0.4}$Co$_{0.6}$MoO$_4$/g-C$_3$N$_4$ was characterized by XRD, FTIR, SEM, and XPS. The catalytic activity of Cu$_{0.4}$Co$_{0.6}$MoO$_4$/g-C$_3$N$_4$ was measured under different temperatures, different catalyst dosages, and different amounts of ammonia borane. It was found that Cu$_{0.4}$Co$_{0.6}$MoO$_4$/g-C$_3$N$_4$ showed the best catalytic activity with a STY value of 75.7 mol$_{H_2}$/mol$_{cat}$ min$^{-1}$. The well-controlled composition and the well-dispersed active substances contributed to the improvement of the catalytic performance.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/9/9/714/s1, Figure S1: XRD patterns of Cu$_x$Co$_{1-x}$MoO$_4$/g-C$_3$N$_4$ ($x = 0, 0.2, 0.6, 0.8, 1$) and Cu$_{0.4}$Co$_{0.6}$MoO$_4$. Figure S2: FTIR pattern of Cu$_x$Co$_{1-x}$MoO$_4$/g-C$_3$N$_4$. Figure S3: EDS spectra of Cu$_x$Co$_{1-x}$MoO$_4$/g-C$_3$N$_4$ for (a) $x = 0$, (b) $x = 0.2$, (c) $x = 0.6$, (d) $x = 0.8$, and (e) $x = 1$ and (f) Cu$_{0.4}$Co$_{0.6}$MoO$_4$. Table S1: Element ratios of Cu, Co, and Mo in Cu$_x$Co$_{1-x}$MoO$_4$/g-C$_3$N$_4$.

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Conflicts of Interest: The authors declare no conflict of interest.

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