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Cu_{0.4}Co_{0.6}MoO₄ 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-efficient and highly reactive catalyst for hydrolyzing AB. Herein, we synthesized a series of Cu_xCo_{1-x}MoO₄ dispersed on graphitic carbon nitride (g-C₃N₄) to dehydrogenate AB. Among those Cu_xCo_{1-x}MoO₄/g-C₃N₄ catalysts, Cu_{0.4}Co_{0.6}MoO₄/g-C₃N₄ exhibited the highest site time yield (STY) value of 75.7 mol_{H₂} 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}MoO₄/g-C₃N₄ was about 4.3 times as high as that for the unsupported Cu_{0.4}Co_{0.6}MoO₄, indicating that the g-C₃N₄ 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}MoO₄/g-C₃N₄ 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 H₂O 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]:

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 ($g\text{-C}_3\text{N}_4$) 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 $g\text{-C}_3\text{N}_4$ as a catalyst support in AB dehydrogenation. For example, Guo et al. designed $g\text{-C}_3\text{N}_4$ -supported Au–Co nanoparticles with a site time yield (STY) value of $28.4 \text{ mol}_{\text{H}_2} \text{ mol}_{\text{cat}}^{-1} \text{ min}^{-1}$ [17]. In contrast, the STY value of Au–Co nanoparticles without $g\text{-C}_3\text{N}_4$ support was only ca. $14 \text{ mol}_{\text{H}_2} \text{ mol}_{\text{cat}}^{-1} \text{ min}^{-1}$. Fan et al. synthesized Rh nanoparticles with an average size of 3.1 nm which dispersed onto $g\text{-C}_3\text{N}_4$. The STY value for the resultant catalysts was $969 \text{ mol}_{\text{H}_2} \text{ mol}_{\text{cat}}^{-1} \text{ min}^{-1}$ [18]. Hamza et al. reported that the STY value of AgPd/ $g\text{-C}_3\text{N}_4$ was $94.1 \text{ mol}_{\text{H}_2} \text{ mol}_{\text{cat}}^{-1} \text{ min}^{-1}$ [19]. Jia et al. synthesized Pb(0) nanoparticles anchored into $g\text{-C}_3\text{N}_4$ with chitosan, and their STY value was $27.7 \text{ mol}_{\text{H}_2} \text{ mol}_{\text{cat}}^{-1} \text{ min}^{-1}$ at 30°C [20]. Fan et al. synthesized AgCo bimetallic nanoparticles supported on $g\text{-C}_3\text{N}_4$, and the STY value of $\text{Ag}_{0.1}\text{Co}_{0.9}/g\text{-C}_3\text{N}_4$ was $249.02 \text{ mol}_{\text{H}_2} \text{ mol}_{\text{cat}}^{-1} \text{ min}^{-1}$ [21]. It should be noted that the applications of $g\text{-C}_3\text{N}_4$ 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 $g\text{-C}_3\text{N}_4$ and investigate their activity in AB dehydrogenation.

Herein, we report a series of $\text{Cu}_x\text{Co}_{1-x}\text{MoO}_4$ supported on $g\text{-C}_3\text{N}_4$ for ammonia borane hydrolysis. As far as we know, a noble-metal-free catalyst supported on $g\text{-C}_3\text{N}_4$ 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 $\text{Cu}_x\text{Co}_{1-x}\text{MoO}_4/g\text{-C}_3\text{N}_4$. It was discovered that $\text{Cu}_{0.4}\text{Co}_{0.6}\text{MoO}_4/g\text{-C}_3\text{N}_4$ shows the best catalytic activity as its STY value can reach $75.7 \text{ mol}_{\text{H}_2} \text{ mol}_{\text{cat}}^{-1} \text{ min}^{-1}$, which is better than the properties of most non-precious metals reported in the literature. In addition, $\text{Cu}_{0.4}\text{Co}_{0.6}\text{MoO}_4/g\text{-C}_3\text{N}_4$ exhibited higher catalytic activity in contrast to the unsupported counterpart, $\text{Cu}_{0.4}\text{Co}_{0.6}\text{MoO}_4$.

2. Results and Discussion

Figure 1 shows the Powder X-ray diffraction (XRD) patterns of $g\text{-C}_3\text{N}_4$ before loading and $\text{Cu}_{0.4}\text{Co}_{0.6}\text{MoO}_4/g\text{-C}_3\text{N}_4$. Evidently, the peaks of $g\text{-C}_3\text{N}_4$, CuMoO_4 , and CoMoO_4 can be found in $\text{Cu}_{0.4}\text{Co}_{0.6}\text{MoO}_4/g\text{-C}_3\text{N}_4$. The diffraction peak at 27.7° can be observed in both XRD patterns and is the characteristic peak of $g\text{-C}_3\text{N}_4$. The diffraction peaks of $\text{Cu}_{0.4}\text{Co}_{0.6}\text{MoO}_4/g\text{-C}_3\text{N}_4$ at 23.4° , 36.5° , 38.6° , 43.1° , and 52.9° correspond to the (110), (002), (200), ($\bar{1}\bar{1}2$), 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_3N_4 , CoMoO_4 , and CuMoO_4 . For comparison, a series of $\text{Cu}_x\text{Co}_{1-x}\text{MoO}_4/g\text{-C}_3\text{N}_4$ were synthesized, and their XRD patterns are shown in Figure S1.

The Fourier transform infrared (FTIR) spectra of $\text{Cu}_{0.4}\text{Co}_{0.6}\text{MoO}_4$, $\text{Cu}_{0.4}\text{Co}_{0.6}\text{MoO}_4/g\text{-C}_3\text{N}_4$, and pure $g\text{-C}_3\text{N}_4$ are shown in Figure 2. For pure $g\text{-C}_3\text{N}_4$ 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 $\text{Cu}_{0.4}\text{Co}_{0.6}\text{MoO}_4/g\text{-C}_3\text{N}_4$, the bands in the range of $1240\text{--}1640 \text{ cm}^{-1}$ correspond to the bonds of pure $g\text{-C}_3\text{N}_4$. In contrast, the bands at 937, 615, and 475 cm^{-1} are assigned to the stretching vibrations of the $t\text{-MoO}_4$ group, Mo=O stretching, and Mo–O–Mo bending vibrations [24–26]. This result further confirms that $\text{Cu}_{0.4}\text{Co}_{0.6}\text{MoO}_4$ nanorods were successfully loaded onto $g\text{-C}_3\text{N}_4$. The FTIR spectra of different $\text{Cu}_x\text{Co}_{1-x}\text{MoO}_4/g\text{-C}_3\text{N}_4$ samples are shown in Figure S2 and are similar to that of $\text{Cu}_{0.4}\text{Co}_{0.6}\text{MoO}_4/g\text{-C}_3\text{N}_4$.

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

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

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 $g\text{-C}_3\text{N}_4$ in Figure 3a is similar to that in a previous report [6]. The unsupported $\text{Cu}_{0.4}\text{Co}_{0.6}\text{MoO}_4$ 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 $\text{Cu}_{0.4}\text{Co}_{0.6}\text{MoO}_4$ well and increase the number of exposed active sites, we introduced $g\text{-C}_3\text{N}_4$ into solution during the synthesis process and successfully obtained the $\text{Cu}_{0.4}\text{Co}_{0.6}\text{MoO}_4/g\text{-C}_3\text{N}_4$ material (Figure 3d,e). The rods could be easily found on the surface of $g\text{-C}_3\text{N}_4$. 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 $g\text{-C}_3\text{N}_4$ into the synthetic system did not change the morphology and size of the $\text{Cu}_{0.4}\text{Co}_{0.6}\text{MoO}_4$ 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 $g\text{-C}_3\text{N}_4$ material, while the elements O, Mo, Co, and Cu result from the $\text{Cu}_{0.4}\text{Co}_{0.6}\text{MoO}_4$. 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 $\text{Cu}_x\text{Co}_{1-x}\text{MoO}_4/g\text{-C}_3\text{N}_4$ are close to the theoretical values.

Figure 3. FESEM images of (a) g-C₃N₄, (b,c) Cu_{0.4}Co_{0.6}MoO₄, and (d,e) Cu_{0.4}Co_{0.6}MoO₄/g-C₃N₄; (f) EDS spectrum of point analysis.

The valence states of the elements in Cu_{0.4}Co_{0.6}MoO₄/g-C₃N₄ 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 sp²-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 Cu²⁺. 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 Mo⁶⁺ [29]. The peak at 531.3 eV in the O 1s spectrum illustrates the existence of O²⁻ [30]. Considering the XRD, SEM, and XPS results together, we can conclude that our obtained product is g-C₃N₄-supported Cu_{0.4}Co_{0.6}MoO₄.

The catalytic activity levels of g-C₃N₄, Cu_{0.4}Co_{0.6}MoO₄, and Cu_{0.4}Co_{0.6}MoO₄/g-C₃N₄ in the hydrolysis of ammonia borane were tested at 293 K. It can be seen in Figure 5 that g-C₃N₄ had no catalytic activity in the hydrolytic reaction. In addition, the catalytic activity of unsupported Cu_{0.4}Co_{0.6}MoO₄ was significantly lower than that of Cu_{0.4}Co_{0.6}MoO₄/g-C₃N₄. The STY values were 75.7 mol_{H₂}mol_{cat}⁻¹ min⁻¹ for Cu_{0.4}Co_{0.6}MoO₄/g-C₃N₄ and 17.6 mol_{H₂}mol_{cat}⁻¹ min⁻¹ for the unsupported Cu_{0.4}Co_{0.6}MoO₄. As discussed above, the introduction of g-C₃N₄ 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}MoO₄/g-C₃N₄ acts as a catalyst. Figure 6 illustrates catalytic hydrolysis on the unsupported Cu_{0.4}Co_{0.6}MoO₄ and Cu_{0.4}Co_{0.6}MoO₄/g-C₃N₄ clearly. We also tried to synthesize ZnMoO₄ by a similar strategy to measure the catalysis activity of other molybdates. The result that there was no catalysis activity in ZnMoO₄ illustrates that molybdates have no reactivity. However, according to the literature, molybdates can serve as a Lewis acid and conduce the adsorption of OH⁻ on the catalyst surface, which would be of benefit to the hydrolysis reaction [31].

Figure 4. XPS pattern of $\text{Cu}_{0.4}\text{Co}_{0.6}\text{MoO}_4/\text{g-C}_3\text{N}_4$: (a) C 1s; (b) N 1s; (c) Co 2p; (d) Cu 2p; (e) Mo 3d; (f) O 1s.

Figure 5. Time vs. $n(\text{H}_2)/n(\text{AB})$ during the catalytic hydrolysis of ammonia borane (AB) with catalysts $\text{Cu}_{0.4}\text{Co}_{0.6}\text{MoO}_4$, $\text{g-C}_3\text{N}_4$ and $\text{Cu}_{0.4}\text{Co}_{0.6}\text{MoO}_4/\text{g-C}_3\text{N}_4$.

Figure 6. Scheme of the catalytic properties of bulk $\text{Cu}_{0.4}\text{Co}_{0.6}\text{MoO}_4$ and $\text{Cu}_{0.4}\text{Co}_{0.6}\text{MoO}_4/\text{g-C}_3\text{N}_4$.

In consideration of variation of the molar ratio of cobalt to copper, we synthesized a series of $\text{Cu}_x\text{Co}_{1-x}\text{MoO}_4/\text{g-C}_3\text{N}_4$ ($x = 0, 0.2, 0.4, 0.6, 0.8, 1$) samples to test their catalytic performance, shown in Figure 7. No matter the value of x , $\text{Cu}_x\text{Co}_{1-x}\text{MoO}_4/\text{g-C}_3\text{N}_4$ samples were active in the hydrolysis of ammonia borane. $\text{CuMoO}_4/\text{g-C}_3\text{N}_4$, without Co element, showed the lowest catalytic activity with a STY value of $11.7 \text{ mol}_{\text{H}_2} \text{mol}_{\text{cat}}^{-1} \text{ min}^{-1}$. 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 $75.7 \text{ mol}_{\text{H}_2} \text{mol}_{\text{cat}}^{-1} \text{ min}^{-1}$. It is worth noting that the STY of $\text{CoMoO}_4/\text{g-C}_3\text{N}_4$ was $35.35 \text{ mol}_{\text{H}_2} \text{mol}_{\text{cat}}^{-1} \text{ min}^{-1}$, which is lower than those of $\text{Cu}_{0.2}\text{Co}_{0.8}\text{MoO}_4/\text{g-C}_3\text{N}_4$, $\text{Cu}_{0.4}\text{Co}_{0.6}\text{MoO}_4/\text{g-C}_3\text{N}_4$, and $\text{Cu}_{0.6}\text{Co}_{0.4}\text{MoO}_4/\text{g-C}_3\text{N}_4$, 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 $3.9 \text{ mol}_{\text{H}_2} \text{mol}_{\text{cat}}^{-1} \text{ min}^{-1}$, respectively; these STY values are lower than those of $\text{CoMoO}_4/\text{g-C}_3\text{N}_4$ and $\text{CuMoO}_4/\text{g-C}_3\text{N}_4$, further confirming that the introduction of $\text{g-C}_3\text{N}_4$ enhanced the catalytic activity.

Figure 7. (a) Time vs. $n(\text{H}_2)/n(\text{AB})$ during the catalytic hydrolysis of AB with catalyst $\text{Cu}_x\text{Co}_{1-x}\text{MoO}_4/\text{g-C}_3\text{N}_4$; (b) STY values with x for $\text{Cu}_x\text{Co}_{1-x}\text{MoO}_4/\text{g-C}_3\text{N}_4$.

To understand the relationship between catalyst dosage and hydrogen production rate, the hydrogen evolution curves for different amounts of $\text{Cu}_{0.4}\text{Co}_{0.6}\text{MoO}_4/\text{g-C}_3\text{N}_4$ are shown in Figure 8. As the amount of $\text{Cu}_{0.4}\text{Co}_{0.6}\text{MoO}_4/\text{g-C}_3\text{N}_4$ increased, the rate of hydrogen production also increased. By fitting the curve of $\ln(\text{catalyst})$ vs. $\ln(\text{rate})$, 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. 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) $n(\text{H}_2)/n(\text{AB})$ vs. reaction time at different $\text{Cu}_{0.4}\text{Co}_{0.6}\text{MoO}_4/\text{g-C}_3\text{N}_4$ 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 $\ln(\text{rate})$ vs. $\ln(\text{NH}_3\text{BH}_3)$ 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 $\text{Cu}_{0.4}\text{Co}_{0.6}\text{MoO}_4/\text{g-C}_3\text{N}_4$ 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 the 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 $\text{Cu}_{0.4}\text{Co}_{0.6}\text{MoO}_4/\text{g-C}_3\text{N}_4$ was as low as $14.46 \text{ kJ mol}^{-1}$. 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 $\text{Cu}_{0.4}\text{Co}_{0.6}\text{MoO}_4/\text{g-C}_3\text{N}_4$. As can be seen, the STY value of $\text{Cu}_{0.4}\text{Co}_{0.6}\text{MoO}_4/\text{g-C}_3\text{N}_4$ is higher than those of most noble-metal-free catalysts in the literature. Therefore, $\text{Cu}_{0.4}\text{Co}_{0.6}\text{MoO}_4/\text{g-C}_3\text{N}_4$ is one of the best potential catalysts for AB hydrolysis.

Figure 10. (a) Hydrogen evolution at different reaction temperatures in the range of 298–313 K; (b) the relationship between logarithm of k and $1/T$.

Table 1. Comparison of the STY value and apparent activation energy of our $\text{Cu}_{0.4}\text{Co}_{0.6}\text{MoO}_4/\text{g-C}_3\text{N}_4$ catalyst with those of some other representative noble-metal-free catalysts in the literature.

Catalysts	STY ($\text{mol}_{\text{H}_2} \text{mol}_{\text{cat}}^{-1} \text{min}^{-1}$)	STY without support ($\text{mol}_{\text{H}_2} \text{mol}_{\text{cat}}^{-1} \text{min}^{-1}$)	E_a (kJ mol^{-1})	Reference
Ni/ZIF-8	85.7	/	28	[33]
$\text{Cu}_{0.5}\text{Co}_{0.5}\text{O-rGO}$	81.7	/	−45.26	[34]
$\text{Cu}_{0.4}\text{Co}_{0.6}\text{MoO}_4/\text{g-C}_3\text{N}_4$	75.7	17.6	14.46	This work
CoP	72.2	/	/	[35]
$\text{Cu}_{0.8}\text{Co}_{0.2}\text{O-GO}$	70.0	/	45.53	[36]
$\text{Ni}_{0.9}\text{Mo}_{0.1}/\text{graphene}$	66.7	2.3	/	[37]
$\text{Co}_{0.8}\text{Cu}_{0.2}\text{MoO}_4$	55	/	/	[32]
$\text{Cu}_{0.49}\text{Co}_{0.51}/\text{C}$	45	/	51.9	[38]
$\text{Cu}_{0.8}\text{Ni}_{0.2}$	41.9	/	40.53	[39]
CuCo/graphene	41	12	54.89	[40]
NiP	40.4	/	44.6	[5]
$\text{Ni}_{91}\text{P}_9/\text{rGO}$	13.3	/	34.7	[41]
$\text{Ni/g-C}_3\text{N}_4$	18.7	/	36	[6]

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 $\text{g-C}_3\text{N}_4$, 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 % $\text{Cu}_x\text{Co}_{1-x}\text{MoO}_4/\text{g-C}_3\text{N}_4$, 0.4 g $\text{g-C}_3\text{N}_4$ 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 $\text{g-C}_3\text{N}_4$ 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 $\text{Cu}_{0.4}\text{Co}_{0.6}\text{MoO}_4$ was also prepared in a similar process to that described above, except that no $\text{g-C}_3\text{N}_4$ 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 K α radiation ($\lambda = 1.5406 \text{ \AA}$) in the range of

$2\theta = 10^{\circ}$ – 80° (Bruker, Billerica, MA, USA). The Fourier transform infrared spectrum (FTIR) was measured to acquire functional group information using a Nicolet 6700 FTIR spectrometer in the range of 450 – 3000 cm^{-1} (ThermoFisher Scientific, Waltham, MA, USA). Microstructures and the EDS spectrum were analyzed using a JEOL-7100F field-emission scanning electron microscope (FESEM) (Jeol Ltd., Akishima, Japan). The elements and oxidation states were analyzed using a Kratos Axis Ultra DLD X-ray photoelectron spectrometer (XPS) (Kratos Analytical, New York, NY, USA). The molar ratios of Cu, Co, and Mo in different samples were determined using an Agilent 7800 inductively coupled plasma mass spectrometer (ICP-MASS) (Agilent Technologies Inc., Santa Clara, CA, USA).

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 $\text{Cu}_x\text{Co}_{1-x}\text{MoO}_4/\text{g-C}_3\text{N}_4$ 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 $\text{Cu}_x\text{Co}_{1-x}\text{MoO}_4/\text{g-C}_3\text{N}_4$ ($x = 0, 0.2, 0.4, 0.6, 0.8, 1$) and unsupported $\text{Cu}_{0.4}\text{Co}_{0.6}\text{MoO}_4$ for the hydrolysis of ammonia borane. As a representative catalyst, $\text{Cu}_{0.4}\text{Co}_{0.6}\text{MoO}_4/\text{g-C}_3\text{N}_4$ was characterized by XRD, FTIR, SEM, and XPS. The catalytic activity of $\text{Cu}_{0.4}\text{Co}_{0.6}\text{MoO}_4/\text{g-C}_3\text{N}_4$ was measured under different temperatures, different catalyst dosages, and different amounts of ammonia borane. It was found that $\text{Cu}_{0.4}\text{Co}_{0.6}\text{MoO}_4/\text{g-C}_3\text{N}_4$ showed the best catalytic activity with a STY value of $75.7\text{ mol}_{\text{H}_2}\text{mol}_{\text{cat}}^{-1}\text{ min}^{-1}$. 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 $\text{Cu}_x\text{Co}_{1-x}\text{MoO}_4/\text{g-C}_3\text{N}_4$ ($x = 0, 0.2, 0.6, 0.8, 1$) and $\text{Cu}_{0.4}\text{Co}_{0.6}\text{MoO}_4$, Figure S2: FTIR pattern of $\text{Cu}_x\text{Co}_{1-x}\text{MoO}_4/\text{g-C}_3\text{N}_4$, Figure S3: EDS spectra of $\text{Cu}_x\text{Co}_{1-x}\text{MoO}_4/\text{g-C}_3\text{N}_4$ for (a) $x = 0$, (b) $x = 0.2$, (c) $x = 0.6$, (d) $x = 0.8$, and (e) $x = 1$ and (f) $\text{Cu}_{0.4}\text{Co}_{0.6}\text{MoO}_4$, Table S1: Element ratios of Cu, Co, and Mo in $\text{Cu}_x\text{Co}_{1-x}\text{MoO}_4/\text{g-C}_3\text{N}_4$.

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References

1. Sartbaeva, A.; Kuznetsov, V.L.; Wells, S.A.; Edwards, P.P. Hydrogen nexus in a sustainable energy future. *Energy Environ. Sci.* **2008**, *1*, 79. [CrossRef]
2. Schlapbach, L.; Züttel, A. Hydrogen-storage materials for mobile applications. *Nature* **2001**, *414*, 353–358. [CrossRef] [PubMed]
3. Jacobson, M.Z.; Colella, W.G.; Golden, D.M. Cleaning the air and improving health with hydrogen fuel-cell vehicles. *Science* **2005**, *308*, 1901–1905. [CrossRef] [PubMed]
4. Liu, C.; Fan, Y.Y.; Liu, M.; Cong, H.T.; Cheng, H.M.; Dresselhaus, M.S. Hydrogen Storage in Single-Walled Carbon Nanotubes at Room Temperature. *Science* **1999**, *286*, 1127–1129. [CrossRef] [PubMed]
5. Peng, C.Y.; Kang, L.; Cao, S.; Chen, Y.; Lin, Z.S.; Fu, W.F. Nanostructured Ni_2P as a Robust Catalyst for the Hydrolytic Dehydrogenation of Ammonia-Borane. *Angew. Chem. Int. Ed. Engl.* **2015**, *54*, 15725–15729. [CrossRef] [PubMed]

6. Gao, M.; Yu, Y.; Yang, W.; Li, J.; Xu, S.; Feng, M.; Li, H. Ni nanoparticles supported on graphitic carbon nitride as visible light catalysts for hydrolytic dehydrogenation of ammonia borane. *Nanoscale* **2019**, *11*, 3506–3513. [[CrossRef](#)] [[PubMed](#)]
7. Peng, B.; Chen, J. Ammonia borane as an efficient and lightweight hydrogen storage medium. *Energy Environ. Sci.* **2008**, *1*, 479–483. [[CrossRef](#)]
8. Wen, M.; Cui, Y.; Kuwahara, Y.; Mori, K.; Yamashita, H. Non-Noble-Metal Nanoparticle Supported on Metal-Organic Framework as an Efficient and Durable Catalyst for Promoting H₂ Production from Ammonia Borane under Visible Light Irradiation. *ACS Appl. Mater. Interfaces* **2016**, *8*, 21278–21284. [[CrossRef](#)] [[PubMed](#)]
9. Lu, D.; Liao, J.; Zhong, S.; Leng, Y.; Ji, S.; Wang, H.; Wang, R.; Li, H. Cu_{0.6}Ni_{0.4}Co₂O₄ nanowires, a novel noble-metal-free catalyst with ultrahigh catalytic activity towards the hydrolysis of ammonia borane for hydrogen production. *Int. J. Hydrog. Energy* **2018**, *43*, 5541–5550. [[CrossRef](#)]
10. Navlani-García, M.; Mori, K.; Nozaki, A.; Kuwahara, Y.; Yamashita, H. Highly efficient Ru/carbon catalysts prepared by pyrolysis of supported Ru complex towards the hydrogen production from ammonia borane. *Appl. Catal. A Gen.* **2016**, *527*, 45–52. [[CrossRef](#)]
11. Chandra, M.; Xu, Q. Room temperature hydrogen generation from aqueous ammonia-borane using noble metal nano-clusters as highly active catalysts. *J. Power Sources* **2007**, *168*, 135–142. [[CrossRef](#)]
12. Jiang, H.L.; Umegaki, T.; Akita, T.; Zhang, X.B.; Haruta, M.; Xu, Q. Bimetallic Au–Ni nanoparticles embedded in SiO₂ nanospheres: Synergetic catalysis in hydrolytic dehydrogenation of ammonia borane. *Chem. Eur. J.* **2010**, *16*, 3132–3137. [[CrossRef](#)] [[PubMed](#)]
13. Chen, G.; Desinan, S.; Rosei, R.; Rosei, F.; Ma, D. Synthesis of Ni–Ru alloy nanoparticles and their high catalytic activity in dehydrogenation of ammonia borane. *Chem. Eur. J.* **2012**, *18*, 7925–7930. [[CrossRef](#)] [[PubMed](#)]
14. Zheng, Y.; Jiao, Y.; Zhu, Y.; Cai, Q.; Vasileff, A.; Li, L.H.; Han, Y.; Chen, Y.; Qiao, S. Molecule-level g-C₃N₄ coordinated transition metals as a new class of electrocatalysts for oxygen electrode reactions. *J. Am. Chem. Soc.* **2017**, *139*, 3336–3339. [[CrossRef](#)] [[PubMed](#)]
15. Li, X.; Wang, X.; Antonietti, M. Solvent-free and metal-free oxidation of toluene using O₂ and g-C₃N₄ with nanopores: Nanostructure boosts the catalytic selectivity. *ACS Catal.* **2012**, *10*, 2082–2086. [[CrossRef](#)]
16. Habibi-Yangjeh, A.; Mousavi, M.; Nakata, K. Boosting visible-light photocatalytic performance of g-C₃N₄/Fe₃O₄ anchored with CoMoO₄ nanoparticles: Novel magnetically recoverable photocatalysts. *J. Photochem. Photobiol. A Chem.* **2019**, *368*, 120–136. [[CrossRef](#)]
17. Guo, L.; Cai, Y.; Ge, J.; Zhang, Y.; Gong, L.; Li, X.; Wang, K.; Ren, Q.; Su, J.; Chen, J. Multifunctional Au-Co@CN Nanocatalyst for Highly Efficient Hydrolysis of Ammonia Borane. *ACS Catal.* **2015**, *5*, 388–392. [[CrossRef](#)]
18. Lu, R.; Hu, M.; Xu, C.; Wang, Y.; Zhang, Y.; Xu, B.; Gao, D.; Bi, J.; Fan, G. Hydrogen evolution from hydrolysis of ammonia borane catalyzed by Rh/g-C₃N₄ under mild conditions. *Int. J. Hydrog. Energy* **2018**, *43*, 7038–7045. [[CrossRef](#)]
19. Kahri, H.; Sevim, M.; Metin, Ö. Enhanced catalytic activity of monodispersed AgPd alloy nanoparticles assembled on mesoporous graphitic carbon nitride for the hydrolytic dehydrogenation of ammonia borane under sunlight. *Nano Res.* **2016**, *10*, 1627–1640. [[CrossRef](#)]
20. Jia, H.; Chen, X.; Song, X.; Zheng, X.; Guan, X.; Liu, P. Graphitic carbon nitride-chitosan composites-anchored palladium nanoparticles as high-performance catalyst for ammonia borane hydrolysis. *Int. J. Energy Res.* **2018**, *43*, 535–543. [[CrossRef](#)]
21. Wang, Q.; Xu, C.; Ming, M.; Yang, Y.; Xu, B.; Wang, Y.; Zhang, Y.; Wu, J.; Fan, G. In Situ Formation of AgCo Stabilized on Graphitic Carbon Nitride and Concomitant Hydrolysis of Ammonia Borane to Hydrogen. *Nanomaterials* **2018**, *8*, 280. [[CrossRef](#)]
22. Lu, D.; Li, J.; Lin, C.; Liao, J.; Feng, Y.; Ding, Z.; Li, Z.; Liu, Q.; Li, H. A Simple and Scalable Route to Synthesize Co_xCu_{1-x}Co₂O₄@Co_yCu_{1-y}Co₂O₄ Yolk-Shell Microspheres, A High-Performance Catalyst to Hydrolyze Ammonia Borane for Hydrogen Production. *Small* **2019**, *15*, e1805460. [[CrossRef](#)] [[PubMed](#)]

23. Wang, S.; Li, D.; Sun, C.; Yang, S.; Guan, Y.; He, H. Synthesis and characterization of g-C₃N₄/Ag₃VO₄ composites with significantly enhanced visible-light photocatalytic activity for triphenylmethane dye degradation. *Appl. Catal. B Environ.* **2014**, *144*, 885–892. [[CrossRef](#)]
24. Cheng, J.; Huang, W. Effect of cobalt (nickel) content on the catalytic performance of molybdenum carbides in dry-methane reforming. *Fuel Process. Technol.* **2010**, *91*, 185–193. [[CrossRef](#)]
25. Amanulla, A.M.; Shahina, S.K.J.; Sundaram, R.; Magdalane, C.M.; Kaviyarasu, K.; Letsholathebe, D.; Mohamed, S.B.; Kennedy, J.; Maaza, M. Antibacterial, magnetic, optical and humidity sensor studies of beta-CoMoO₄-Co₃O₄ nanocomposites and its synthesis and characterization. *J. Photochem. Photobiol. B* **2018**, *183*, 233–241. [[CrossRef](#)] [[PubMed](#)]
26. Tan, H.; Chen, W.; Liu, D.; Feng, X.; Li, Y.; Yan, A.; Wang, E. Two diphosphonate-functionalized asymmetric polyoxomolybdates with catalytic activity for oxidation of benzyl alcohol to benzaldehyde. *Dalton Trans.* **2011**, *40*, 8414–8418. [[CrossRef](#)] [[PubMed](#)]
27. Li, C.; Du, Y.; Wang, D.; Yin, S.; Tu, W.; Chen, Z.; Kraft, M.; Chen, G.; Xu, R. Unique P–Co–N Surface Bonding States Constructed on g-C₃N₄ Nanosheets for Drastically Enhanced Photocatalytic Activity of H₂ Evolution. *Adv. Funct. Mater.* **2017**, *27*, 1604328. [[CrossRef](#)]
28. Li, Q.; Li, Y.; Zhao, J.; Zhao, S.; Zhou, J.; Chen, C.; Tao, K.; Liu, R.; Han, L. Ultrathin nanosheet-assembled hollow microplate CoMoO₄ array derived from metal-organic framework for supercapacitor with ultrahigh areal capacitance. *J. Power Sources* **2019**, *430*, 51–59. [[CrossRef](#)]
29. Yu, M.Q.; Jiang, L.X.; Yang, H.G. Ultrathin nanosheets constructed CoMoO₄ porous flowers with high activity for electrocatalytic oxygen evolution. *Chem. Commun.* **2015**, *51*, 14361–14364. [[CrossRef](#)] [[PubMed](#)]
30. Yu, B.; Jiang, G.; Xu, W.; Cao, C.; Liu, Y.; Lei, N.; Evariste, U.; Ma, P. Construction of NiMoO₄/CoMoO₄ nanorod arrays wrapped by Ni-Co-S nanosheets on carbon cloth as high performance electrode for supercapacitor. *J. Alloys Compd.* **2019**, *799*, 415–424. [[CrossRef](#)]
31. Fernandes, R.; Patel, N.; Miotello, A.; Calliar, L. Co–Mo–B–P Alloy with Enhanced Catalytic Properties for H₂ Production by Hydrolysis of Ammonia Borane. *Top. Catal.* **2012**, *55*, 1032–1039. [[CrossRef](#)]
32. Liao, J.; Lu, D.; Diao, G.; Zhang, X.; Zhao, M.; Li, H. Co_{0.8}Cu_{0.2}MoO₄ Microspheres Composed of Nanoplatelets as a Robust Catalyst for the Hydrolysis of Ammonia Borane. *ACS Sustain. Chem. Eng.* **2018**, *6*, 5843–5851. [[CrossRef](#)]
33. Wang, C.; Tuninetti, J.; Wang, Z.; Zhang, C.; Ciganda, R.; Salmon, L.; Moya, S.; Ruiz, J.; Astruc, D. Hydrolysis of ammonia-borane over Ni/ZIF-8 nanocatalyst: High efficiency, mechanism and controlled hydrogen release. *J. Am. Chem. Soc.* **2017**, *139*, 11610. [[CrossRef](#)] [[PubMed](#)]
34. Zheng, H.; Feng, K.; Shang, Y.; Kang, Z.; Sun, X.; Zhong, J. Cube-Like CuCoO Nanostructures on Reduced Graphene Oxide for H₂ Generation from Ammonia Borane. *Inorg. Chem. Front.* **2018**, *5*, 1180. [[CrossRef](#)]
35. Fu, Z.C.; Xu, Y.; Chan, S.L.; Wang, W.W.; Li, F.; Liang, F.; Chen, Y.; Lin, Z.S.; Fu, W.F.; Che, C.M. Highly efficient hydrolysis of ammonia borane by anion (OH[−], F[−], Cl[−])-tuned interactions between reactant molecules and CoP nanoparticles. *Chem. Commun.* **2017**, *53*, 705–708. [[CrossRef](#)] [[PubMed](#)]
36. Feng, K.; Zhong, J.; Zhao, B.; Zhang, H.; Xu, L.; Sun, X.; Lee, S.T. Cu_xCo_{1−x}O Nanoparticles on Graphene Oxide as A Synergistic Catalyst for High-Efficiency Hydrolysis of Ammonia–Borane. *Angew. Chem. Int. Ed. Engl.* **2016**, *55*, 11950–11954. [[CrossRef](#)] [[PubMed](#)]
37. Yao, Q.; Lu, Z.-H.; Huang, W.; Chen, X.; Zhu, J. High Pt-like activity of the Ni–Mo/graphene catalyst for hydrogen evolution from hydrolysis of ammonia borane. *J. Mater. Chem. A* **2016**, *4*, 8579–8583. [[CrossRef](#)]
38. Bulut, A.; Yurderi, M.; Ertas, İ.E.; Celebi, M.; Kaya, M.; Zahmakiran, M. Carbon dispersed copper-cobalt alloy nanoparticles: A cost-effective heterogeneous catalyst with exceptional performance in the hydrolytic dehydrogenation of ammonia-borane. *Appl. Catal. B Environ.* **2016**, *180*, 121–129. [[CrossRef](#)]
39. Zhang, J.; Li, H.; Zhang, H.; Zhu, Y.; Mi, G. Poreously hierarchical Cu@Ni cubic-cage microstructure: Very active and durable catalyst for hydrolytically liberating H₂ gas from ammonia borane. *Renew. Energy* **2016**, *99*, 1038–1045. [[CrossRef](#)]

40. Song, F.Z.; Zhu, Q.L.; Yang, X.C.; Xu, Q. Monodispersed CuCo Nanoparticles Supported on DiamineFunctionalized Graphene as a Non-noble Metal Catalyst for Hydrolytic Dehydrogenation of Ammonia Borane. *ChemNanoMat* **2016**, *2*, 942–945. [[CrossRef](#)]
41. Du, X.; Yang, C.; Zeng, X.; Wu, T.; Zhou, Y.; Cai, P.; Cheng, G.; Luo, W. Amorphous NiP supported on rGO for superior hydrogen generation from hydrolysis of ammonia borane. *Int. J. Hydrog. Energy* **2017**, *42*, 14181–14187. [[CrossRef](#)]

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