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Graphical abstract



A noble-metal-free catalyst has been firstly developed to achieve excellent catalytic activity and 100% H₂ selectivity toward hydrogen generation from hydrazine borane.

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Hydrazine borane (N₂H₄BH₃, 15.4 wt% H) has been considered as a high potential hydrogen storage material because of inherent advantages such as its high hydrogen content and high stability in the solid state. However, the practical application of N₂H₄BH₃ for generation of hydrogen is strongly inhibited by the need of expensive noble metal-based catalysts. To overcome this challenge, noble-metal-free CuNiMo nanocatalysts were prepared using a facile chemical reduction approach under ambient atmosphere at room temperature. Unexpectedly, the resultant CuNiMo catalyst exhibits excellent catalytic activity, and 100% H₂ selectivity toward hydrogen generation from N₂H₄BH₃ via its BH₃ group hydrolysis and N₂H₄ moiety decomposition at 323 K. To the best of our knowledge, this is the first report that a noble-metal-free catalyst can achieve a complete conversion of N₂H₄BH₃ to H₂. In addition, CuNiMo catalyst may be attributed to the electronic modification among Cu, Ni and Mo, and also related to the strong basic site of the Cu_{0.4}Ni_{0.6}Mo. The present simple, low cost, highly efficient, and highly selective catalyst may promote the practical application of N₂H₄BH₃ as an effective hydrogen storage material.

1. Introduction

Hydrogen is generally proposed to be a promising efficient energy carrier and an environmentally attractive fuel for future energy application because of its high energy density and efficiency with a low environmental load.¹⁻⁵ However, controlled storage and release of hydrogen are the well-known technological barriers in achieving a hydrogen economy socity.⁶⁻⁹ Recently, the chemical storage of hydrogen was considered as an effective way for practical applications. Among the variety types of chemical hydrogen storage materials, ammonia borane (NH₃BH₃) is attractive due to its high hydrogen content (19.6 wt% H).¹⁰⁻¹⁴ Since the mid-2000s, many efforts have been paid on the catalytic hydrolysis of NH₃BH₃ (eqn 1) at room temperature.^{10,11} However, the catalytic dehydrogenation of the NH3 group in NH3BH3 is thermodynamically impossible under ambient conditions, which makes the effective gravimetric hydrogen storage

capacity (GHSC) of NH₃BH₃-4H₂O decrease to 5.9 wt% H. In recent years, hydrous hydrazine (N₂H₄·H₂O) has been regarded as a promising liquid-phase hydrogen storage material owing to the high hydrogen content (8.0 wt % H).¹⁵⁻²⁰ This material could be released by complete decomposition of hydrazine to H₂ and N₂ (eqn 2), giving the effective GHSC as high as 8.0 wt % H, whereas the safety issues (e.g., volatility, corrosivity, toxicity, and etc.) need to be solved for practical application.

$NH_3BH_3 + 4H_2O \rightarrow NH_4B(OH)_4 + 3H_2$	(1)
$N_2H_4 \rightarrow N_2 + 2H_2$	(2)
$3N_2H_4 \rightarrow 4NH_3 + N_2$	(3)
$N_2H_4BH_3 + 3H_2O \rightarrow N_2H_4 + B(OH)_3 + 3H_2$	(4)

Hydrazine borane (N₂H₄BH₃, 15.4 wt% H), a derivative of NH₃BH₃ where N₂H₄ group have substituted NH₃ group, has been regarded as a competitive candidate for chemical hydrogen storage material.²¹⁻³² N₂H₄BH₃ is also a safe and stable solid material under ambient condition. This material can be easily prepared by mixing hydrazine hemisulfate and sodium borohydride in dioxane at room temperature.²² In comparison with the themolysis of $N_2H_4BH_3$ to release H_2 , where high temperature is required and the rate of H_2 generation is low, the catalytic hydrolysis of N₂H₄BH₃ can proceed rapidly under mild conditions.^{21,33-35} Like for NH₃BH₃, the BH₃ group in $N_2H_4BH_3$ is able to readily hydrolyze in the presence of a suitable catalyst (eqn 4). The hydrolysis of N₂H₄BH₃ was firstly reported by Özkar and co-workers, which only focused on the hydrolysis of the BH_3 group (3 equiv. H_2 , eqn 3).³³ However, unlike the NH₃ moiety of NH₃BH₃, the N₂H₄

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Page 2 of 9

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ARTICLE

moiety in N₂H₄BH₃ can also be dehydrogenated to H₂ and N₂ over a selective catalyst (eqn 2). Hence, hydrogen stored in N₂H₄BH₃ could be ideally dehydrogenated into 5 mol H₂ and 1 mol N₂ per mol NH₃BH₃ in the presence of a selective catalyst. In this case, the effective GHSC of the N₂H₄BH₃-3H₂O system becomes up to 10.0 wt%, which is much higher than those of benchmark hydrogen systems NH₃BH₃-4H₂O (5.9 wt% H)⁴⁰⁻⁵⁰ and N₂H₄·H₂O (8.0 wt% H).¹⁵⁻²⁰ The combination of these unique advantages makes N₂H₄BH₃ and N₂H₄·H₂O.

However, to maximize the usability of N₂H₄BH₃ as a hydrogen storage material, the undesired incomplete decomposition to NH₃ (eqn 3) must be avoided and the catalyst should be economically viable. To this end, extensive efforts have been undertaken to develop an effective catalytic system to realize the selectively dehydrogenation of N₂H₄BH₃. The first achievement by Demirci and Xu was that 5.79 equivalents of $H_2 + N_2$ per $N_2H_4BH_3$ can be released in the participation of $Ni_{0.89}Pt_{0.11} NPs$.²⁴ Although the H₂ selectivity of these catalysts has been greatly improved, the catalytic activities are still too low, mainly due to the sluggish kinetics during the decomposition of N₂H₄ moiety in N₂H₄BH₃. Recent works have shown that Ni_{0.6}Pt_{0.4}/MSC-30 and Rh_{0.8}Ni_{0.2}@CeO_x/rGO catalysts can lead to complete conversion of $N_2H_4BH_3$ to H_2 with high activity. 29,30 Despite great progress made in recent years, however, all the reported heterogeneous catalysts up to now involve noble metal,²⁴⁻³² which greatly limits their large scale practical applications due to their high cost and insufficient reserves in the earth's crust. Therefore, the development of the noble-metal-free catalyst with high activity and superior selectivity for complete conversion of $N_2H_4BH_3$ to H_2 is imperative.

Herein, we report a facile approach to synthesizing the noble-metal-free CuNiMo nanocatalyst that shows a favorable catalytic activity, 100% H₂ selectivity, as well as robust durability for hydrogen generation from N₂H₄BH₃ in an alkaline solution, with which 6 equiv. (H₂ + N₂) per N₂H₄BH₃ can be released within 13.9 min at 323 K. To best of our knowledge, this is the first report that noble-metal-free catalyst can achieve the complete conversion of N₂H₄BH₃ to H₂ via hydrolysis of the BH₃ moiety and decomposition of the N₂H₄ moiety.

2. Experimental

2.1 Chemicals and materials

Hydrazine borane (N₂H₄BH₃) was synthesized according to our previous reported procedure.³⁰⁻³² Other chemicals were obtained from commercial available and used without further purification. Copper chloride dihydrate (CuCl₂·2H₂O, Sinopharm Chemical Reagent Co. Ltd., >99%), nickel chloride hexahydrate (NiCl₂·6H₂O, Sinopharm Chemical Reagent Co. Ltd., >98%), cobalt chloride hexahydrate(CoCl₂·6H₂O, Sinopharm Chemical Reagent Co. Ltd., >99%), Iron sulfate heptahydrate (FeSO₄·6H₂O, Sinopharm Chemical Reagent Co. Ltd., >99%) sodium molybdate dihydrate (Na₂MoO₄·2H₂O, J&K Scientific Ltd., >99.5%), sodium borohydride (NaBH₄, Aldrich, 99%), sodium hydroxide (NaOH, Tianjin Fuchen Chemical Reagent, >96%), hydrazine monohydrate (N₂H₄·H₂O, Aladdin, 98%) were used as received. Ultrapure water with the specific resistance of 18.3 M Ω ·cm was obtained by reversed osmosis followed by ion exchange and filtration.

2.2 Catalysts characterization

Powder X-ray diffraction (XRD) measurements were carried on a Rigaku RINT-2000 X-ray diffractometer with a Cu anode, operating at 40 kV and 40 mA. Transmission electron microscope (TEM, JEM-2010) and scanning transmission electron microscope (STEM, Titan G2 60-300) equipped with energy dispersive X-ray (EDX) mapping were applied for the detailed microstructure of the synthesized samples. The TEM samples were dispersed in ethanol with sonication for 20 min to get well-dispersed, and one or two droplets of the nanoparticles suspension were dropped onto the amorphous carbon coated copper grid. Chemical compositions of the catalysts were determined by an inductively coupled plasma (ICP) spectrophotometer (Varian, 725-ES). X-ray photoelectron spectroscopy (XPS) was acquired after Ar sputtering for 5 min with an ESCALABMKLL X-ray photoelectron spectrometer using monochromatized AI Ka excitation. Temperature programmed desorption of CO₂ (CO₂-TPD) experiments were performed on a Micromeritics AutoChem II 2920 automated apparatus using a thermal conductivity detector (TCD). The UV-vis absorption spectra were recorded on a UV-vis spectrophotometer (UV-vis, Hitachi, U-3310). For the UV-Vis measurements, ethanol (25 mL), concentrated hydrochloric acid (2.5 mL, 1 M), and 0.5 g paradimethylaminobenzaldehyde (PDAB, 0.5 g) were mixed together as the chromogenic agent for $N_2H_4BH_3$. Next, 5 mg $N_2H_4BH_3$, 1 mL hydrochloric acid (1 mol L⁻¹), and 50 mL deionized water were mixed together as the solution A and stored for 12 h before measurements. Then, 0.1 mL of solutions A, 2 mL chromogenic agent, and 25 mL de-ionized water were mixed, and the sample solutions were stored for 30 min before measurements.

2.3 Preparation of catalysts

Synthesis of Cu_{0.4}Ni_{0.6}Mo catalyst: The Cu_{0.4}Ni_{0.6}Mo catalyst was synthesized by using a facile one-step reduction method at room temperature. Typically, 6.89 mg of CuCl₂·2H₂O (0.04 mmol), 14.55 mg of NiCl₂·6H₂O (0.06 mmol), and 24.45 mg of Na₂MoO₄·2H₂O (0.1 mmol) were dissolved in 4 mL of water. Then, 1 mL aqueous solution of NaBH₄ (30 mg) were rapid added into the above mixture solution with vigorous stirring until the bubble generation ceased. Finally, the black product of Cu_{0.4}Ni_{0.6}Mo catalyst was obtained.

Synthesis of Cu_{0.4}Ni_{0.6}Mo_x catalyst: The Cu_{0.4}Ni_{0.6}Mox with different molar contents of Mo (x = Mo/(Cu+Ni); x = 0, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, and 1.4) were synthesized using the above method by changing the addition content of Na₂MoO₄, and keeping the molar content of Cu+Ni to be 0.1 mmol.

Synthesis of Cu_{1-y}Ni_yMo catalyst: The Cu_{1-y}Ni_yMo NPs with different compositions of Cu and Ni (y = 0, 0.2, 0.4, 0.5, 0.6, 0.7, 0.8, and 1.0) were prepared using the similar method as for

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the $Cu_{0.4}Ni_{0.6}Mo$ catalyst by changing the molar contents of Cu and Ni, and keeping the molar content of Mo to be 0.1 mmol.

Synthesis of monometallic Cu, Ni, and Mo catalyst: An analogous synthesized procedure was followed as above to prepare CuNiMo by using only 34.35 mg of $CuCl_2 \cdot 2H_2O$ (0.2 mmol), 48.50 mg of NiCl_2·6H_2O (0.2 mmol) and 48.9 mg of Na₂MoO₄·2H₂O (0.2 mmol), respectively, for the preparation of monometallic Cu, Ni, and Mo catalyst.

Synthesis of M_1M_2Mo (M_1 or M_2 = Fe, Co, Ni, Cu) catalysts: M_1M_2Mo (M_1 or M_2 = Fe, Co, Ni, Cu) nanocatalysts were prepared by using a synthetic methodology similar to that for CuNiMo.

2.4 Catalytic activities for hydrogen generation from N₂H₄BH₃

Typically, the aqueous solution (5 mL) containing $Cu_{0.4}Ni_{0.6}Mo$ catalyst (n_{metal} = 0.2 mmol) and NaOH (2.0 M) were placed in a two-necked round-bottomed flask (50 mL) sealed with a silicon septum. One neck of the flask was connected to a gas burette to measure the volume of the released gas. The reactor was immersed in a water bath to maintain a constant temperature of 323 K. The catalytic reaction started when the N₂H₄BH₃ (1.0 mmol) was added into the flask with vigorous stirring. The gas released from the reaction was passed through a hydrochloric acid solution (1.0 M) before being measured volumetrically. The reaction was completed when there was no more gas evolved. The selectivity (α) of hydrogen for N₂H₄BH₃ dehydrogenation was determined on the basis of the equation: $N_2H_4BH_3 + 3H_2O \rightarrow B(OH)_3 + (3+2\alpha)H_2 + (2\alpha+1)/3N_2 + 4(1-2\alpha+1)/3N_2 + 4(1-2\alpha+1)/3N_2$ α)/3NH₃, which can be derived from the eqn (2), (3), and (4). Therefore, the selectivity (α) is calculated to be as the following equation (eqn 5):

$$\alpha = \frac{3\lambda \cdot 10}{8} \left[\lambda = \frac{n(H_2 + N_2)}{n(N_2H_4BH_3)} \left(\frac{10}{3} \le \lambda \le 6 \right) \right] \quad (5)$$

The catalytic activities of other catalysts for hydrogen generation from $N_2H_4BH_3$ were also applied as the above method.

For the durability test, after the catalytic dehydrogenation of $N_2H_4BH_3$ was completed, another equivalent of $N_2H_4BH_3$ (1 mmol) was subsequently added to the flask to initiate the reaction. It should be mentioned that before the durability test, an excess amount of NaOH (5.0 M) was added into the reaction system to neutralize the hydrolysate (H₃BO₃) formed during the first step (the hydrolysis BH₃ moiety) of $N_2H_4BH_3$ dehydrogenation.^{30,32} Such cycle experiments of the catalyst were repeated for 10 times at 323 K.

2.5 Catalytic activities for hydrogen generation from N₂H₄·H₂O

The catalytic activities of Cu_{0.4}Ni_{0.6}Mo NPs for hydrogen generation from N₂H₄·H₂O (1 mmol) were also applied as the above method for N₂H₄BH₃.

3. Results and discussion

3.1 Synthesis and characterization of catalysts

The catalysts of CuNiMo were synthesized using a facile onestep approach at room temperature, in which, CuCl₂·2H₂O, NiCl₂·6H₂O, and Na₂MoO₄·2H₂O were used as the metal precursors and NaBH₄ was added as the reducing agent. The as-synthesized CuNiMo catalysts could be separated from the reaction solution by centrifugation, washed with water, and dried in vacuum oven at 313 K. The compositions of the assynthesized CuNiMo catalysts were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Obviously, the molar ratios of Cu : Ni: Mo are in good agreement with its initial values (Table S1). Among all the assynthesized samples, the optimized Cu_{0.4}Ni_{0.6}Mo NPs exhibited the highest activity (*vide infra*), and therefore Cu_{0.4}Ni_{0.6}Mo catalyst was chosen as the model catalyst for full characterization.

The morphologies and size of as-synthesized Cu_{0.4}Ni_{0.6}Mo NPs were investigated by transmission electron microscopy (TEM). The Cu_{0.4}Ni_{0.6}Mo NPs are well dispersed with a mean particle size of about 5.9 ± 1.2 nm (Fig. 1a,b and Fig. S1). In sharp contrast, without the addition of Mo, the Cu_{0.4}Ni_{0.6} NPs are aggregated to a larger size of about 21.8 ± 5.7 nm (Fig. 1d and Fig. S2c), which clearly demonstrates that the introduction of Mo into $Cu_{0.4}Ni_{0.6}$ NPs can induce the reduction of the metal NP size. In addition, it is found that the size of the $Cu_{0.4}Ni_{0.6}Mo_x$ NPs decreases with increasing the Mo content (Fig. 1 and Fig. S2). The high-angle annular dark-field scanning TEM (HAADF-STEM) and elemental mapping images were taken out to examine the distribution of Cu, Ni, and Mo in the Ni-Cu_{0.4}Ni_{0.6}Mo NPs (Fig. 1d). It can be clearly seen that Cu, Ni, and Mo are homogeneously distributed in the metal nanoparticles (Fig. 1c). In addition, from the selected-area electron diffraction (SAED) patterns, it can be find that the sample of Cu_{0.4}Ni_{0.6}Mo is in an amorphous state (Fig. 1a, inset),



Fig. 1 (a) TEM image and the corresponding SAED pattern, (b) particle size distribution, and (c) HAADF-STEM image and the corresponding elemental mapping images of $Cu_{0.4}Ni_{0.6}MO$ NPs. (d) TEM image and the corresponding SAED pattern of $Cu_{0.4}Ni_{0.6}$ NPs.

Journal of Materials Chemistry A Accepted Manuscrip



Fig. 2 X-ray diffraction patterns of $Cu_{0.4}Ni_{0.6}$ NPs and $Cu_{0.4}Ni_{0.6}Mo$ NPs before and after heat treatment at 823 K for 3 h under Ar atmosphere in tube furnace.

while that the $Cu_{0.4}Ni_{0.6}$ sample is polycrystalline (Fig. 1d, inset, which were further confirmed by the high-resolution TEM images (HRTEM, inset of Fig. S2a) and the powder X-ray diffraction (XRD) patterns (Fig. 2, *vide infra*). Therefore, the formation of the amorphous phase of $Cu_{0.4}Ni_{0.6}Mo$ catalyst may be attributed to the presence of Mo in this sample.

The crystalline structures of the as-synthesized catalysts were further characterized by XRD. As exhibited in Fig. 2, the XRD pattern of the Cu_{0.4}Ni_{0.6}Mo shows no obvious diffraction peak (red trace), indicating that the sample is in an amorphous state, which are consistent with its SAED and HRTEM results (inset of Fig. 1a and Fig. S1). While the sample prepared without Mo has an obvious crystalline peak at around $2\theta = 43.64^{\circ}$ (Fig. 2, blue trace), which is in an intermediate position between the (111) plane of fcc Cu (JCPDS: 04-0836 and the (111) plane of fcc Ni (JCPDS: 04-0850), confirming the alloy structure of Cu_{0.4}Ni_{0.6} NPs. After heat treatment at 873 K for 3



Fig. 3 XPS spectra of (a) Cu 2p, (b) Ni 2p, (c) Mo 3d, and (d) CO₂-TPD mass spectra for the Cu_{0.4}Ni_{0.6}Mo and Cu_{0.4}Ni_{0.6} NPs.

h in Ar atmosphere, the sample of $Cu_{0.4}Ni_{0.6}Mo$ NPs is well crystallized. As revealed in Fig. 2 (black trace), the peaks at around $2\theta = 43.70^{\circ}$, 50.78° , and 74.89° are assigned to CuNi alloy. The rest of peaks shown in Fig. 2 (black trace) can be easily indexed to the Mo (JCPSD: 65-7442), MoO_2 (JCPSD: 65-5787), and MoO_3 (JCPSD: 05-0508), respectively. Based on the above analyses, Mo-modified CuNi alloy NPs have been successfully prepared through the present facile chemical reduction method.

The X-ray photoelectron spectroscopy (XPS) analyses after Ar sputtering for Cu_{0.4}Ni_{0.6}Mo and Cu_{0.4}Ni_{0.6} NPs were performed to understand the electronic states and surface interaction among Cu, Ni, and Mo. From the XPS spectra, it is apparent that Cu (Fig. 3a) and Ni (Fig. 3b) are present in metallic state. The Mo species in $Cu_{0.4}Ni_{0.6}Mo$ NPs (Fig. 3c) are found to exist in the form of metallic (Mo, 228.46 eV) and oxidation state (MoO₂, 229.52 eV; MoO₃, 233.41 eV), which is probably due to the fact that Mo ions are difficult to be reduced. In addition, it can be seen that the addition of Mo into Cu_{0.4}Ni_{0.6} NPs results in changes of the binding energy. The binding energies for Cu 2p (Fig. 3a) and Ni 2p (Fig. 3b) in Cu_{0.4}Ni_{0.6}Mo NPs are both shifted to the lower binding energies compared with those in Cu_{0.4}Ni_{0.6} NPs, respectively, while, the binding energy for metallic Mo in Cu_{0.4}Ni_{0.6}Mo NPs (228.57 eV) is shifted to a higher binding energy compared with that of standard state of metallic Mo (228.0 eV). These shifts demonstrated that some electrons were transferred from Mo to Cu and Ni in the sample of Cu_{0.4}Ni_{0.6}Mo. Such modified electron structure in Cu_{0.4}Ni_{0.6}Mo could have the potential to enhance the catalytic activity for hydrogen generation from N₂H₄BH₃. From the CO₂-TPD measurements, we can clearly see that the strength of basic sites of the Cu_{0.4}Ni_{0.6}Mo NPs is higher than that of the Cu_{0.4}Ni_{0.6} NPs (Fig. 3d and Fig. S4). And the basic sites of the Cu_{0.4}Ni_{0.6}Mo_x NPs tend to gradually strengthen with the increase of Mo content (Fig. S4a). As the strong basic site is known to be beneficial to the selective cleavage of the N-H bond in the decomposition of N_2H_4 of $N_{2}H_{4}BH_{3},^{51\text{-}56}$ thus the $Cu_{0.4}Ni_{0.6}Mo$ NPs may have high selectivity towards the dehydrogenation of N₂H₄BH₃ (vide



Fig. 4 Time-course plots for the dehydrogenation of N₂H₄BH₃ aqueous solution (0.2 M, 5 mL) catalyzed by different catalysts in the presence of NaOH (2.0 M) at 323 K ($n_{metal}/n_{N_2H_4BH_3} = 0.2$).

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The catalytic performance of the Cu_{0.4}Ni_{0.6}Mo NPs toward the dehydrogenation of N₂H₄BH₃ was evaluated in a typical water-filled graduated buret system and compared with the Cu, Ni, Mo, $Cu_{0.4}Ni_{0.6}$, CuMo, and NiMo NPs. Remarkably, the Cu_{0.4}Ni_{0.6}Mo NPs exhibited the highest activity among all the catalysts prepared in this work, with which 6.0 equivalents (H₂ + N_2) per $N_2H_4BH_3$ (100% selectivity calculated by eqn 5) can be released within only 13.9 min at 323 K (Fig. 4 and Table S2). As for the NiMo NPs, 5.1 equivalents of gas can be released within 18.1 min, whereas the CuMo and Cu_{0.4}Ni_{0.6}Mo NPs showed much lower H_2 selectively, with which only 3.3 equivalents of gas were evolved, respectively. Both monometallic Cu and Ni NPs showed activity for the hydrolysis of BH₃ group only, and 3.0 equivalents of gas can be generated from the aqueous N₂H₄BH₃ solution, respectively (Fig. 4 and Table S2). Pure Mo had no catalytic activity, but the presence of it was clearly found to play an essential role in the synthesis of highly active Cu_{0.4}Ni_{0.6}Mox NPs (Fig. S5). Even adding a small amount of Mo to $Cu_{0.4}Ni_{0.6}$ had a significant effect on the activity and hydrogen selectivity, and the optimal molar ratio of $X_{MO} = n_{MO}/n_{(Cu+Ni)}$ was determined to be 1.0. In addition, the catalytic performance of $Cu_{1-y}Ni_yMo$ was also affected by the molar ratio of Cu/Ni. When the molar content of Mo was set as the value of 1.0, the optimum Cu : Ni molar ratio was 0.4 : 0.6 (Fig. S6). Increasing or decreasing the optimum value can result in the loss of the catalytic activity. After catalytic reaction over $Cu_{0.4}Ni_{0.6}Mo$ NPs, the absence of $N_2H_4BH_3$ in ultraviolet visible (UV-vis) spectrum further confirmed the completeness of the dehydrogenation of N₂H₄BH₃ (Fig. S7). The total turnover frequency (TOF) of $Cu_{0.4}Ni_{0.6}Mo$ was calculated to be 108 $h^{\text{-1}}$ at 323 K, a very high value among reported catalysts (Table S3).²⁴⁻³² To best of our knowledge, this is the first report that noble-metal-free catalyst can catalyze the complete dehydrogenation of $N_2H_4BH_3$. The excellent catalytic activities of Cu_{0.4}Ni_{0.6}Mo NPs could be attributed to the electronic modification among Cu, Ni and Mo, and also related to the small particle size of Cu_{0.4}Ni_{0.6}Mo NPs. Besides the above mentioned factors, the strong basic site of the



Fig. 5 Catalytic dehydrogenation of N₂H₄BH₃ aqueous solution (0.2 M, 5 mL) to generated H₂ over different catalysts in the presence of NaOH (2.0 M) at 323 K ($n_{metal}/n_{N_2H_4BH_3} = 0.2$).

 $Cu_{0.4}Ni_{0.6}Mo$ NPs is another factor contributing to the high activity for the hydrogen generation from the hydrolysis of $N_2H_4BH_3$ (Fig. 3d).

Since the addition of Mo could effectively enhance the activity and selectivity of CuNiMo NPs, Mo-modified other non-noble-metal catalysts were also prepared by the same method as CuNiMo NPs, and their catalytic performances for hydrogen generation from N₂H₄BH₃ were investigated and compared (Fig. 5, Fig. S8-S12, and Table S2). As shown in Fig. 5, the Fe_{0.4}Ni_{0.6}Mo catalysts also exhibited excellent activities with which 6.0 equiv. $(H_2 + N_2)$ can be released, whereas $Co_{0.4}Ni_{0.6}Mo$ nanoparticles showed 5.6 equiv. (H₂ + N₂) for hydrogen generation from N₂H₄BH₃ under analogous reaction conditions. In contrast to the high catalytic performance of the Ni-based catalyst, other components of catalysts obtained by different non-noble metals (e.g., Cu_{0.4}Co_{0.6}Mo) exhibited much lower catalytic activity (4.4 equiv. gases), whereas the Cu_{0.4}Fe_{0.6}Mo catalyst was found to be only active in the hydrolysis of BH₃ group in N₂H₄BH₃ (3.0 equiv. H₂) under our reaction conditions. The above results indicate that the H₂ selectivity of all the Mo-modified non-noble metal catalysts except CuFeMo NPs (Fig. 5) is remarkably improved compared with their unmodified counterparts (Fig. S13).

Alkali was used as an effective promoter for hydrogen generation from $N_2H_4BH_3$ in the presence of catalyst. As illustrated in Fig. 6, the H_2 selectivity and activity of the $Cu_{0.4}Ni_{0.6}Mo$ NPs increased rapidly until the concentration of NaOH went up to 2.0 M, after which further increasing the NaOH content had no influence on the dehydrogenation of





Fig. 7 (a) Time-course plots for the dehydrogenation of $N_2H_4BH_3$ aqueous solution (0.2 M, 5 mL) catalyzed by $Cu_{0.4}Ni_{0.6}Mo$ catalysts in the presence of NaOH (2.0 M) at different temperatures ($n_{metal}/n_{N_2H_4BH_3} = 0.2$); (b) Plot of ln k versus 1/T for hydrogen generation from hydrolysis of the BH₃ group (Part 1) and decomposition of the N₂H₄ moiety of N₂H₄BH₃ (Part 2).

 $N_2H_4BH_3$. The possible reason for the promotion effect of alkaline can be understood as follows: (a) the existence of OH^- could reduce the amount of undesirable $N_2H_5^+$ ($N_2H_5^+ + OH^- \rightarrow N_2H_4 + H_2O$) in aqueous solution and promote the rate-determining deprotonation step ($N_2H_4 \rightarrow N_2H_3^* + H^*$) along the decomposition process of N_2H_4 to H_2 and N_2 ; (b) the strong alkaline solution can also help to inhibit the production of NH_3 and thereby raise the H_2 selectivity.^{29-32,51-56}

The reaction temperature also greatly affected the catalytic activities. With increasing reaction temperature, the activities



Fig. 8 Durability test for the dehydrogenation of N₂H₄BH₃ aqueous solution (0.2 M, 5 mL) catalyzed by Cu_{0.4}Ni_{0.6}Mo NPs with NaOH (5.0 M) at 323 K ($n_{metal}/nN_2H_4BH_3 = 0.2$).

of catalyst were further enhanced (Fig. 7a). Although hydrogen in $N_2H_4BH_3$ can not be completely released with the Cu_{0.4}Ni_{0.6}Mo NPs at room temperature (Fig. 7a), the gas released can reach up to 5.53 equiv. $(H_2 + N_2)$ per $N_2H_4BH_3$. The catalytic reactions for hydrogen generation from N₂H₄BH₃ were completed within 37.7, 24.8, 13.9, 8.0, and 3.1 min at 303, 313, 323, 333, and 343 K, respectively, corresponding to TOF values of 37, 59, 108, 187, and 484 h^{-1} . In addition, the increment of reaction rates in each curve (Fig. 7a) showed signs of slowdown with the increase of time, because the hydrolysis of BH₃ group (Part 1 in Fig. 7a and Fig. S14) proceeded more quickly and easily than the decomposition of the N₂H₄ group (Part 2 in Fig. 7a) in N₂H₄BH₃, in consistent with the previous reports.¹⁷⁻²⁵ The values of rate constant k at different temperatures were calculated from the slope of the linear part of each plot in Part 1 and Part 2 from Fig. 7a. According to the Arrhenius plot of In k versus 1/T, the activation energies of the hydrolysis of the BH₃ group (Part 1) and the decomposition of N₂H₄ moiety (Part 2) of N₂H₄BH₃ are calculated to be 19.8 kJ mol⁻¹ (E_{a1} , Fig. 7b) and 54.7 kJ mol⁻¹ $(E_{a2}, Fig. 7b)$, respectively. In addition, the activity of Cu_{0.4}Ni_{0.6}Mo catalyst after heat treatment was also studied. As shown in Fig. S15, the Cu_{0.4}Ni_{0.6}Mo NPs after heat treatment (at 823 K for 3 h in Ar atmosphere) showed a lower catalytic activity and selectivity for hydrogen generation from N₂H₄BH₃ than that of without heat treatment, which is attributed to the Cu04Ni06Mo NPs tend to sinter into larger species at high temperature as evidenced by TEM observation (12.0 nm, Fig. S16).

DOI: 10.1039/C7TA10886A

Journal Name

The Cu_{0.4}Ni_{0.6}Mo NPs was also used as a catalyst to decompose the same amount of N_2H_4 as that result from the second step of the $N_2H_4BH_3$ dehydrogenation reaction. As shown in Fig. S17a, the complete decomposition of N_2H_4 · H_2O over Cu_{0.4}Ni_{0.6}Mo NPs at 323 K can finish in 15.5 min with TOF of 38.7 h⁻¹, which are comparable to those of state-of-the-art catalysts.^{15-20,51-56} In addition, the activation energy for the decomposition of N_2H_4 ·H₂O was estimated to be 56.6 kJ mol⁻¹ (Fig. S17b), which is higher than to that of Cu_{0.4}Ni_{0.6}Mo for the dehydrogenation of the N₂H₄ moiety in N₂H₄BH₃ (E_{a2} = 54.7 kJ mol⁻¹). Based on the above results, it can be found that the Cu_{0.4}Ni_{0.6}Mo catalyst showed a lower catalytic activity for hydrogen generation from N_2H_4 · H_2O than that from $N_2H_4BH_3$. A possible explanation is that the rapid hydrolysis of BH₃ group of N₂H₄BH₃ may accelerate the resulting N₂H₄ moieties interact with the $Cu_{0.4}Ni_{0.6}Mo$ catalyst, thus promoting the $N_2H_4BH_3$ dehydrogenation kinetics. Similar reaction kinetics were observed in the previous stduies.^{29,30}

Finally, we examined the durability of the $Cu_{0.4}Ni_{0.6}Mo$ catalyst, which is very important for further practical application. The durability test was carried out by successively addition an additional aliquot of $N_2H_4BH_3$ into the reaction flask when the previous run was completed. As shown in Fig. 8, the catalytic activity of $Cu_{0.4}Ni_{0.6}Mo$ catalyst is essentially retained until even after ten runs, whereas the reaction rate showed a slight decrease. After the durability test, the $Cu_{0.4}Ni_{0.6}Mo$ catalyst was then characterized by XRD and TEM techniques. The results show that the XRD patterns showing

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ARTICLE

the unchanged nanostructure (Fig. S18), while the TEM image showed the increase of metal size (9.5 nm, Fig. S19). Thus, the slightly decrease in the activity can be ascribed to the increased metal size and the deactivation effect of the increasing metaborate, which accumulates during the hydrolysis of BH_3 group of $N_2H_4BH_3$.

Conclusions

Journal Name

In summary, noble-metal-free based CuNiMo catalysts have been facilely prepared via a simple *in-situ* approach at room temperature under ambient atmosphere. The optimized Cu_{0.4}Ni_{0.6}Mo catalyst showed excellent catalytic activity and 100% H₂ selectivity for the dehydrogenation of N₂H₄BH₃ in an alkaline solution at 323 K. As far as we know, this is the first report in which noble-metal-free catalyst can catalyze the complete dehydrogenation of N₂H₄BH₃. In addition, similar catalysts FeNiMo, CoNiMo, and CuCoMo also show good activity for hydrogen evolution from N₂H₄BH₃. This remarkable improvement of catalytic performance of the noble-metal-free heterogeneous catalysts demonstrates a promising strategy towards the development of N₂H₄BH₃ as a feasible chemical hydrogen storage material in fuel cell application.

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