

Highly Dispersed Surfactant-Free Amorphous NiCoB Nanoparticles and Their Remarkable Catalytic Activity for Hydrogen Generation from Ammonia Borane Dehydrogenation

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Received: 24 January 2018 / Accepted: 24 March 2018 © Springer Science+Business Media, LLC, part of Springer Nature 2018

Abstract

The effective storage and generation of hydrogen at room temperature is an important issue in many areas, including alternative energy. In this work, NiCoB nanoalloys with high B contents, clean surfaces, and good dispersions are synthesized by an in-situ reduction method. The NiCoB catalyst with high B content exhibits significantly more excellent catalytic activity for hydrogen generation from the hydrolytic of ammonia borane than NiCoB catalyst with low B content. The remarkable catalytic performance is attributed to the strong electronic interaction between the incorporated B and the active metal sites of Co and Ni, the clean surface and good dispersion of the catalyst. Basically, the physical and catalytic properties of the catalyst take advantage of the selection of reductant used during the in-situ synthesis of the NiCoB nanoalloys. This work demonstrates that this facile synthetic method is a promising avenue for the rational design of various B incorporated metal catalysts for hydrogen energy exploitation, metal/air batteries, and electrochemical sensors.

Graphical Abstract



Keywords B incorporated nickel-cobalt alloy \cdot In-situ reduction \cdot Heterogeneous catalysis \cdot Hydrogen generation \cdot Ammonia borane

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1 Introduction

Secure and efficient hydrogen storage and generation remains one of the critical technical barriers to hydrogen energy applications [1-3]. Currently, it is of great importance to the exploration of proper chemical hydrogen storage materials that can release hydrogen through in-situ processes under mild conditions for direct usage in fuel cells [4, 5]. Ammonia borane (NH₃BH₃, AB) has been widely regarded as a promising candidate for chemical hydrogen storage applications due to its high hydrogen content of 19.6 wt%, nontoxicity, and high stability at room temperature [6, 7]. AB can release hydrogen through pyrolysis, solvolysis in protic solvents (i.e., hydrolysis or methanolysis), and dehydrocoupling in nonprotic solvents [8–12]. Since pyrolysis requires high temperatures [8], methanolysis and dehydrogenation in organic liquids are not environmentally friendly [11, 12], and the rates of hydrogen release of the above methods are typically relatively low [13], the hydrolysis of AB is considered to be the most promising process because as much as 3 equiv. of hydrogen can be released from AB with appropriate catalysts under mild conditions, according to the equation below:

 $NH_3BH_3 + 2H_2O \rightarrow NH_4^+ + BO_2^- + 3H_2$

In early research, noble metal nanoparticles (NPs), such as Pt, Ru, and Pd, were the most widely investigated catalysts for AB dehydrogenation systems due to their superior catalytic performances [14–17]. However, the NPs' limited abundance and high cost restrict their practical applications [18]. Subsequently, transition metal catalysts, such as Fe, Co, and Ni, have been explored [19-21], and Co was commonly observed to exhibit higher catalytic activity than Fe and Ni [22], though Co is relatively more scarce and higher in cost than two others. To further improve the catalytic activity and simultaneously minimize the cost of the catalysts, combination Co with Fe (or Ni) has attracted much attention [23–25]. Furthermore, nanomaterials containing iron family elements usually possess good stability in catalysis applications because of the easy magnetic separation, which facilitates the recovery of such catalysts [26]. In this sense, magnetic nanoalloys as catalysts are expected to own the advantages of both nanoalloys and magnetic nanomaterials with better catalytic activities than their counterparts and easy magnetic recovery.

It has been reported that with their high concentration of coordinative unsaturated sites and tunable compositions, amorphous catalysts exhibit relatively unique physical and chemical properties compared to crystalline materials [27]. As one of the most promising catalysts, an amorphous metal-boron (B) alloy is applied as an advanced material for petrochemical production, energy conversion and environmental catalysis [28]. For amorphous metal-B alloy catalyst, the bonding structure is intrinsically different from its crystalline counterpart because of the covalent component of its metal-metalloid bonds [29]. This property would result in the occurrence of an electron effect between the metal atoms and the B atoms, which may further promote their catalytic performance [30]. Moreover, the incorporation of B into transition metal catalyst can effectively enhance the catalytic performance [31–34]. Therefore, the preparation of amorphous CoB-based catalysts with different B contents and a comparison of their catalytic performances for hydrogen generation from the hydrolysis of AB are both of great interest.

Non-noble metal NPs with ultrafine sizes have attracted great interest because of their increased surface areas and the adequate number of edge and corner atoms, which greatly improve their catalytic performances. However, non-noble metal NPs with ultrafine sizes are easily aggregated because of their high surface energies and therefore lead to low catalytic activities [35]. To avoid this aggregation, strong surfactants are usually employed to maintain minimization and high dispersion of NPs [36]. However, an overly strong affiliation of surfactants to the NPs may decrease the number of active sites on the surface of NPs, and thus cause the severe deactivation of the NPs [37, 38]. In this sense, employing weak surfactants to guarantee the clean surface and high concentration of active sites of the NPs, while using weak reductants to ensure the good dispersion of the NPs during the slow nucleation process is an appropriate approach that may effectively improve the catalytic performance of the NPs.

In this study, amorphous CoNiB NPs possessing high B contents (CoNiB-*h*) are successfully synthesized by a very facile in-situ reduction method employing AB and NaBH₄ as reductants. The resultant CoNiB-*h* catalyst without any surfactants and supports exhibits uniform dispersion and high activity for the hydrolysis dehydrogenation of AB at 298 K. The total turnover frequency (TOF) obtained by $Co_{0.7}Ni_{0.3}B$ -*h* is much higher than that of ex-situ prepared $Co_{0.7}Ni_{0.3}B$ ($Co_{0.7}Ni_{0.3}B$ -*l*), the latter exhibited obvious aggregation and possessed low content of B. It is interesting that tuning the content of B and the dispersion of NPs through the adoption of different synthesis methods leads to remarkable enhancement of the activity for the hydrolytic dehydrogenation of AB.

2 Experimental Details

2.1 Chemicals

Ammonia borane (NH₃BH₃, Aldrich, 90%), cobalt(II) chloride hexahydrate(CoCl₂·6H₂O, Sinopharm Chemical Reagent Co., Ltd, >99%), nickel (II) chloride hexahydrate

(NiCl₂·6H₂O, Sinopharm Chemical Reagent Co., Ltd, >98%), iron (II) sulfate heptahydrate (FeSO₄·7H₂O, Sinopharm Chemical Reagent Co., Ltd, >99%), hexadecyltrimethyl ammonium bromide (CTAB, Aladdin Chemistry Co., Ltd, >99%), and sodium borohydride (NaBH₄, Sinopharm Chemical Reagent Co., Ltd, >96%) were used as received without any purification.

2.2 Synthesis and Catalytic Study

The CoNiB-*h* catalyst was prepared via an in-situ reduction method using AB and NaBH₄ as reductants. Typically, for $Co_{0.7}Ni_{0.3}B$ -*h* NPs, 10.8 mg of CoCl₂ and 4.7 mg of NiCl₂ were dissolved in 10 ml of distilled water (with a conductivity of 1 µS cm⁻¹). 55.0 mg of AB and 8.0 mg NaBH₄ were kept in a two-necked round-bottom flask. One neck was connected to a gas burette, and the other was connected to a pressure-equalization funnel to introduce 10 ml of aqueous solution containing certain contents of CoCl₂ and NiCl₂. Once the aqueous solution was added to AB and NaBH₄ under vigorously stirring, the black suspension appeared immediately, and the H₂ generated at the meantime. The reaction was completed until there was no more gas generated. The evolution of gas was monitored by using the gas burette.

The CoNiB-*l* catalyst was prepared via an ex-situ reduction method using NaBH₄ as a reductant. For Co_{0.7}Ni_{0.3}B-*l*, the preparation procedure is same as Co_{0.7}Ni_{0.3}B-*h* except that using NaBH₄ as a reductant. Once the metal NPs generated, the aqueous solution of AB was then introduced into the above solution containing the as-prepared metal NPs to start its catalytic hydrolysis reaction. The Co_{0.7}Ni_{0.3}B stabilized by CTAB was prepared by the similar method to ex-situ reduction process, except mixed 20 mg CTAB with 10 ml aqueous solution of CoCl₂ and NiCl₂. Furthermore, to exclude the impact of metal ions (which may be leached from the catalyst) on the observed activity, the catalytic performance of Co²⁺ and Ni²⁺ salts in the presence of AB has been applied, wherein only AB was employed as a reductant.

For comparison, $Fe_{0.5}Co_{0.5}B-h$ NPs and $Fe_{0.5}Ni_{0.5}B-h$ NPs were also prepared by the same method as $Co_{0.7}Ni_{0.3}B-h$.

CoNiB-*h* NPs with different Co and Ni compositions, which labeled as $Co_x Ni_{1-x}B-h$, were also synthesized by a similar method shown above. The x value in $Co_x Ni_{1-x}B-h$ was changed from 0 to 1.0 (x = 0, 0.1, 0.3, 0.5, 0.7, 0.9, 1.0). Notably, molar ratio of $(Co^{2+} + Ni^{2+})$: AB was 0.04 for all reactions.

To analyze activation energy of this reaction, a series of experiments were carried out at different temperatures (298, 303, 308, and 313 K) with $\text{Co}_{0.7}\text{Ni}_{0.3}\text{B-}h$ under ambient atmosphere.

To study the stability of the $\text{Co}_{0.7}\text{Ni}_{0.3}\text{B-}h$, after the first hydrogen generation reaction completed, another equivalent of

AB aqueous solution (0.16 M, 10 ml) was added to the flask to regenerate hydrogen. The evolution of gas was monitored by the gas burette. Such recycle experiments with $Co_{0.7}Ni_{0.3}B$ -*h* was repeated 4 times under ambient atmosphere at room temperature.

2.3 Calculation Methods

The turnover frequency (TOF) reported here was total TOF values based on the measured mole number of metal contents in catalysts, which was calculated from the equation as follow:

$$TOF = \frac{P_{atm}V_{H_2}/RT}{n_{metal}t}$$
(1)

where TOF is the total turnover frequency, P_{atm} is the atmospheric pressure, V_{H2} is the volume of the generated H₂ corresponding to the whole process of hydrolysis of AB, R is the universal gas constant, *T* is the room temperature (298 K), n_{metal} is the measured mole number of metal catalyst by ICP-OES, and *t* is the reaction time from the beginning of the AB hydrolysis reaction to the end.

The relationship between the temperature and the hydrogen generation rate (corresponding to 50% conversion) was followed Arrhenius behavior. The Arrhenius' reaction rate equation can be written as follows:

$$\ln k = \ln A - E_a / RT \tag{2}$$

where A is the reaction constant.

2.4 Characterization

X-ray diffraction (XRD) was performed on a Rigaku RINT-2000 X-ray diffractometer with Cu K α radiation (λ = 1.54056 Å). Transmission electron microscope (TEM, Tecnai F20, Philips) and corresponding energy-dispersive X-ray spectroscopy (EDS) were applied to analyze microstructures and compositions of the specimens. TEM and EDS samples were prepared by depositing one or two droplets of the nanoparticle suspensions onto the amorphous carbon-coated copper grids, which were dried in an argon atmosphere. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) measurements were performed on a Thermo Jarrell Ash (TJA) Atomscan Advantage instrument. X-ray photoelectron spectroscopy (XPS) spectra were acquired with an ESCAL-ABMKLL (Vacuum Generators) spectrometer using Al K α X-rays (240 W).

3 Results and Discussion

3.1 Synthesis and Characterization

The $Co_{0.7}Ni_{0.3}B$ -*h* NPs were synthesized by a one-step insitu reduction method at 298 K. Mixed metal ions of Co^{2+} and Ni²⁺ were used as the metal precursors, and AB and NaBH₄ were added as the reducing agent. For comparison, $Co_{0.7}Ni_{0.3}B$ -*l* NPs were prepared by the same method, except only NaBH₄ was used as a reductant. This method is referred to as the ex-situ reduction method. The as-prepared NPs have been isolated from solutions by centrifugation for characterization.

The phase structures and crystallinities of two samples were first characterized by X-ray diffraction (XRD). As shown in Fig. 1a, b, no peaks are observed in Co_{0.7}Ni_{0.3}B-h and Co_{0.7}Ni_{0.3}B-l, indicating that Co_{0.7}Ni_{0.3}B-h and Co_{0.7}Ni_{0.3}B-l are amorphous. After heat treating at 773 K for 3 h in argon, three obvious peaks are observed between the (111) plane of face-centered cubic (fcc) Co (JCPDS: 15-0806) and the (111) plane of fcc Ni (JCPDS: 04-0850) [23, 39] (Fig. 1c, d). Thus, both samples are reasonably deduced to be Co_{0.7}Ni_{0.3}B crystalline nanoalloys after annealing. Interestingly, compared to the Co_{0.7}Ni_{0.3}B-l (Fig. 1d), the diffraction peaks are slightly shifted to the lower angles for Co_{0.7}Ni_{0.3}B-h (Fig. 1c). These slight expansions of the CoNi lattice may be attributed to a certain number of B atoms being incorporated into the inter-lattice spaces of CoNi nanoalloy [34]. It should be noted that no Co(Ni)₂B or Co(Ni)₃(BO₃)₂ were formed during the reduction reaction, even after the heat treatment of the samples at 773 K for 3 h in argon according to the XRD patterns.



Fig.1 X-ray diffraction patterns of $\text{Co}_{0.7}\text{Ni}_{0.3}\text{B}$ -*h* before (*a*) and after (*c*) heat treatment at 773 K for 3 h in argon atmosphere; and $\text{Co}_{0.7}\text{Ni}_{0.3}\text{B}$ -*l* before (*b*) and after (*d*) heat treatment at 773 K for 3 h in argon atmosphere

Inductively coupled plasma-optical emission spectroscopy (ICP-OES) furnished the accurate element analysis in the asprepared $Co_{0.7}Ni_{0.3}B$ -*h* and $Co_{0.7}Ni_{0.3}B$ -*l* NPs. Through the measured ppm values of Co, Ni, and B, the accurate molar ratio of Co/Ni/B is determined to be 0.401:0.175:0.424 in $Co_{0.7}Ni_{0.3}B$ -*h*, and 0.489:0.212:0.299 in $Co_{0.7}Ni_{0.3}B$ -*l* (Table 1). It is found that the B contents in the two samples are quite different, revealing that the B content could be regulated by different reduction methods.

According to previous reports, B atoms may serve as electron donors to optimize the electronic structure of other metal atoms for dehydrogenation reactions [28]. To investigate the effect of B on the electronic structure of Co and Ni (the crucial active elements for the AB hydrolysis dehydrogenation reaction), X-ray photoelectron spectroscopy (XPS) measurements were performed to identify the electronic states of Ni and Co in Co_{0.7}Ni_{0.3}B-h and Co_{0.7}Ni_{0.3}B-l and the valence state of B in the $Co_{0.7}Ni_{0.3}B-h$ sample (Fig. 2). A thin oxidized layer formed during the exposure of the sample to air in the XPS sample preparation process, with binding energies for Ni $2p_{3/2}$ and $2p_{1/2}$ at 856.2 and 873.6 eV, respectively. Meanwhile, the binding energies for Ni $2p_{3/2}$ and $2p_{1/2}$ at 852.1 eV and 869.5 eV, respectively, can be attributed to Ni⁰. Notably, the Ni binding energies of $Co_{0.7}Ni_{0.3}B-h$ are shifted negatively compared to those of $Co_{0.7}Ni_{0.3}B$ -l (Fig. 2a), and a similar electronic state is present in the Co binding energies (Fig. 2b). After argon etching, the surface oxidation layers of both specimens are removed, the Ni⁰ and Co⁰ binding energies in Co_{0.7}Ni_{0.3}B-hare also shifted to the lower values compared with those in Co_{0.7}Ni_{0.3}B-l (Fig. 2c, d). These shifts demonstrate that compared to Co_{0.7}Ni_{0.3}B-l, more effective electrons transfer from B to Ni (or Co) after a larger number of B atoms are incorporated into $Co_{0.7}Ni_{0.3}B-h$. Thus, it is reasonable to deduce that Co_{0.7}Ni_{0.3}B-h with electron-enriched active sites (Ni and Co sites) is favorable to the catalytic hydrolytic dehydrogenation of AB [40]. In addition, the B element in $Co_{0.7}Ni_{0.3}B-h$ is in the metallic and oxidized state before argon etching; however, only a peak with a binding energy of 187.5 eV corresponds to B^0 was observed after argon sputtering for 5 min (Fig. 2e), which indicates that no boron oxides (BO_x) or B ions existed in the as-prepared sample. Furthermore, no oxygen and chlorine elements are found by XPS, corresponding to the sample is in an alloy state of CoNiB but

Table 1 The contents of Co, Ni and B in $Co_{0.7}Ni_{0.3}B$ -*h* and $Co_{0.7}Ni_{0.3}B$ -*l* NPs

Samples	ppm (mg l ⁻¹)			Measured value of Co:Ni:B
	Co	Ni	В	
Co _{0.7} Ni _{0.3} B-h	23.632	10.271	4.584	0.401:0.175:0.424
Co _{0.7} Ni _{0.3} B- <i>l</i>	28.818	12.443	3.232	0.489:0.212:0.299



Fig.2 XPS spectra **a** before and **c** after argon etching of Ni 2p, **b** before and **d** after argon etching of Co 2p for $Co_{0.7}Ni_{0.3}B$ -h and $Co_{0.7}Ni_{0.3}B$ -h NPs, **e** B 1s, **f** O 1s, **g** Cl 2p for $Co_{0.7}Ni_{0.3}B$ -h NPs

not in its oxides or chlorides state (Fig. 2f, g). On the basis of the above arguments and XPS results, we suggest that an effective electron effect should occur in $Co_{0.7}Ni_{0.3}B-h$, which is contained with a high B content.

In addition to the different B contents of these two samples, the difference in their states of dispersion in the aqueous solution should be considered. The difference of dispersion between the two samples can be apparently observed by transmission electron microscopy (TEM) images. As shown in Fig. 3a, the Co_{0.7}Ni_{0.3}B-l NPs appear severely agglomerated. The dispersion of the Co_{0.7}Ni_{0.3}B-l NPs can be improved by the introduction of strong surfactant [41]. This is confirmed by the fact that an analogous experiment with a stronger surfactant, such as CTAB, resulted in highly dispersed Co_{0.7}Ni_{0.3}B-l NPs (Fig. 3b). In contrast, the $Co_{0.7}Ni_{0.3}B$ -h NPs are highly dispersed and the surface of NPs is relatively clean (Fig. 3c). It can be reasonably explained that NPs may have rapid nucleation and growth when reduced by a strong reductant and thus may easily agglomerate, despite the addition of a strong surfactant to facilitate the dispersion of the NPs, long chain structure of the surfactant causes the surfaces of the NPs to not be clean [37, 38]. Therefore, employing a reductant with a moderate reducing ability to control the nucleation and growth rate of the NPs while simultaneously using a weak surfactant to disperse the NPs to guarantee their clean surfaces is of great importance. AB, can not only serve as a weak reductant [42], but also as an efficient weak surfactant with a mild affiliation for stabilizing the NPs [19]. It is more appropriate as a reductant than others for the synthesis of highly dispersed surfactant-free amorphous CoNiB NPs in aqueous solution.

The crystal structures of the as-prepared samples were further characterized by selected-area electron diffraction (SAED) patterns. As shown in Fig. 3, the $Co_{0.7}Ni_{0.3}B$ -1 and $Co_{0.7}Ni_{0.3}B$ -h are both in an amorphous state, which is consistent with the XRD results. Moreover, the two typical samples have similar particle sizes (less than 5 nm) (Fig. 3b, c). The corresponding energy dispersive X-ray spectroscopy (EDS) spectra confirm the rough atomic ratio of Co: Ni to be 65.10:34.90 for $Co_{0.7}Ni_{0.3}B$ -h (Fig. 3d, trace 1) and 71.20:28.80 for $Co_{0.7}Ni_{0.3}B$ -l (Fig. 3d, trace 2), which is in good agreement with the ICP results.

3.2 Catalytic Activity and Activation Energy

The catalytic performances of $Co_{0.7}Ni_{0.3}B-h$ and $Co_{0.7}Ni_{0.3}B-l$ for H₂ generation from the hydrolysis dehydrogenation of AB at 298 K under ambient atmosphere are presented in Fig. 4. Both of the catalysts exhibit good catalytic activities, this is attributed to the amorphous structures of the two catalysts. It is generally known that amorphous structures possess much more structure distortions and thus provide considerably higher concentrations of surface reactive sites to elevate the activities of nanocatalysts compared to the corresponding crystalline counterparts [43, 44]. Interestingly, the $Co_{0.7}Ni_{0.3}B-h$ with high B content displays much higher catalytic activity than that of $Co_{0.7}Ni_{0.3}B-l$ with low B content. With the



Fig. 3 a TEM image for $Co_{0.7}Ni_{0.3}B-l$ NPs, TEM and SAED (inset) images for **b** $Co_{0.7}Ni_{0.3}B-l$ NPs stabilized by CTAB and **c** $Co_{0.7}Ni_{0.3}B-h$ NPs, **d** the corresponding EDS spectrum for (1) $Co_{0.7}Ni_{0.3}B-h$ NPs and (2) $Co_{0.7}Ni_{0.3}B-l$ NPs



Fig. 4 Time-course plots for the hydrolysis of AB in the presence of (*a*) $Co_{0,7}Ni_{0,3}B-h$, (*b*) $Co_{0,7}Ni_{0,3}B-l$, (*c*) CTAB stabilized $Co_{0,7}Ni_{0,3}B-l$ catalysts and (*d*) the mixed solution of Co^{2+} and Ni^{2+} salts in the presence of AB at room temperature

Co_{0.7}Ni_{0.3}B-*h*, the AB releases its stoichiometric amount (3.0 equiv.) of gases within only 3.5 min at 298 K, and the total TOF is calculated (Eq. 1) to be 30.9 mol(H₂)·mol(metal)⁻¹·min⁻¹, which is comparable to most of the reported non-noble metal catalysts for the hydrolysis of AB to H₂ at the same experimental conditions (Table 2) [10, 20, 45–55]. Whereas for the Co_{0.7}Ni_{0.3}B-*l*, a much longer time (18.5 min) is required to complete the same reaction (Fig. 4b), and the total TOF is only 4.3 mol(H₂)·mol(metal)⁻¹·min⁻¹. This finding demonstrates that catalysts with high B contents can exhibit superior catalytic performance towards hydrogen generation reaction from the AB hydrolysis dehydrogenation, which is attributed to the electrons transfer from B to Ni (and Co) that provides electron-enriched Ni (and Co) sites, thereby contributing

to the hydrolysis reaction by providing the charges to promote the H atom separation from the catalyst surface [40].

It is worth mentioning that except the B contents of $Co_{0.7}Ni_{0.3}B-h$ and $Co_{0.7}Ni_{0.3}B-l$ are different, the difference between their dispersion states in the aqueous solution should also be considered. As seen from Fig. 4a, b, the $Co_{0.7}Ni_{0.3}B-h$ exhibits a catalytic performance superior to that of the $Co_{0.7}Ni_{0.3}B-l$, which is ascribed to the good dispersion and clean surface of the Co_{0.7}Ni_{0.3}B-h. Although the dispersion state of Co_{0.7}Ni_{0.3}B-l has been improved by the addition of a surfactant (Fig. 3b), the catalytic activity of the Co_{0.7}Ni_{0.3}B-l NPs stabilized by CTAB is still inferior to that of the $Co_{0.7}Ni_{0.3}B-h$ (Fig. 4a, c), which can be explained as follows: the strong affiliation of the strong surfactant to the surface of the NPs may decrease the number of active sites and thus cause severe deactivation of the NPs in catalytic reactions [37, 38]. Thus, we conclude that high B content, clean surface, and good dispersion play the significant role in promoting the catalytic activities of nanocatalysts for H₂ generation from hydrolytic dehydrogenation of AB, and the usage of AB as a mild reductant has contributed to the preparation of amorphous CoNiB catalyst with high B content, clean surface, and good dispersion. Moreover, to exclude the impact of metal ions on the observed activity, the reaction which only employed AB as reductant was performed. As a result, the metal ions show no activity at all (Fig. 4d), which might due to the fact that AB with weak reducing ability could not reduce the Co²⁺ and Ni²⁺ salts within a short time. Namely, without washing the catalysts during catalytic tests, the potable leached metal ions are not responsible for the observed catalytic activity. It should be noted that the hydrogen evolution curves are consisted of two parts (Fig. 4b, c). The fast one is contributed to the hydrolysis

Catalyst	Temp. (K)	$n_{catalyst}/n_{AB}$	t (min)	$TOF(min^{-1})$	Ref.
Cu _{0.2} Co _{0.8} /HPC	298	0.158	3.5	6.3	[45]
Cu@FeNi	298	0.040	12.0	8.2	[20]
Cu _{0.3} @Fe _{0.1} Co _{0.6}	298	0.100	3.5	10.5	[46]
Cu _{0.4} @Co _{0.5} Ni _{0.1}	298	0.040	7.5	14.0	[47]
Cu _{0.1} @Co _{0.45} Ni _{0.45} /graphene	298	0.040	7.8	15.46	[48]
Cu ₃ Co ₇ @MIL-101	293	0.034	4.5	19.6	[49]
Cu ₂ Ni ₁ @MIL-101	298	0.500	4.0	20.9	[50]
Cu _{0.5} Co _{0.5} /PDDA-HNT	298	0.090	5.8	30.8	[51]
Co _{0.7} Ni _{0.3} B- <i>h</i>	298	0.036	3.5	30.9	This study
NiCo/MIL-101-U	298	0.020	3.0	44.3	[52]
Cu _{0.49} Co _{0.51} /C	298	0.033	5.8	45.0	[53]
CuCo/MIL-101-1-U	298	0.020	3	51.7	[52]
NiCo/ g-C ₃ N ₄	298	0.020	2.6	53.6	[54]
Rh ₁₅ Ni ₈₅ @ZIF-8	298	0.100	1.5	58.8	[55]
Ni _{0.9} Mo _{0.1} /graphene	298	0.050	0.9	66.7	[10]

Table 2Activities in termsof TOF values of differentnanocatalysts containing Coor Ni tested for hydrogengeneration from hydrolysis ofAB aqueous solution

of NaBH₄, which releases 18 mL gases (4.0 equiv.) [56], and the slow one is contributed to the hydrolysis of AB, which releases 107 mL gases (3.0 equiv.). However, this phenomenon is not obviously observed in Fig. 4a. This is because the rapid hydrogen generation from hydrolysis of AB can occur when $Co_{0.7}Ni_{0.3}B-h$ is used as a catalyst.

To confirm that the in-situ NPs have higher catalytic activities than that of ex-situ NPs, the non-noble metal Fe was used as a substitute for Ni or Co to form FeCoB NPs and FeNiB NPs. As expected, the catalytic performance of the in-situ FeCoB NPs is notably better than that of the ex-situ FeCoB NPs (Fig. 5a). A similar result can also be observed when the AB hydrolysis reactions are catalyzed by FeNiB NPs prepared by the different reduction methods (Fig. 5b). These results demonstrate that the catalytic performance of

catalyst for the hydrolytic dehydrogenation of AB can be greatly improved by an in-situ reduction method.

An investigation of the catalytic performance of CoNiB-*h* nanocatalysts with various Co/Ni molar ratios for AB hydrolysis at 298 K was also performed, and it suggests that the catalytic performance of CoNiB-*h* catalyst significantly depends on its composition (Fig. 6a). Notably, without a Co addition (x = 0), NiB shows the lowest catalytic activity, only giving a total TOF value of 4.7 min⁻¹. When the molar ratio of Co (x value) is increased to 0.7, the TOF value increases to 30.9 min⁻¹. Further increasing the Co molar ratio from 0.7 to 0.9, only a slight enhancement in TOF can be obtained (Fig. 6b). Even though when the molar ratio of Co reaches 1.0 (CoB), the reaction efficiency is only slightly superior



Fig.5 a Time-course plots for the hydrolysis of AB catalyzed by (1) in-situ $Fe_{0.5}Co_{0.5}B$ and (2) ex-situ $Fe_{0.5}Co_{0.5}B$ catalysts; **b** Time-course plots for the hydrolysis of AB catalyzed by (1) in-situ



 $Fe_{0.5}Ni_{0.5}B$ and (2) ex-situ $Fe_{0.5}Ni_{0.5}B$ catalysts at room temperature under ambient atmosphere



Fig.6 a Time-course plots for the hydrolysis of AB catalyzed by $Co_x Ni_{1-x}B-h$ NPs with different *x* values under ambient atmosphere at room temperature, **b** The effect of Co/Ni molar ratios on the total TOF values

to the $\text{Co}_{0.7}\text{Ni}_{0.3}\text{B-h}$ nanocatalyst. Compared to the NiB, the catalytic role of Co element in CoNiB-*h* nanoalloy is synergistic with Ni, which can effectively adjust the surface electronic states of nanocatalysts, especially with the local strain on the surface and the number of effective atomic coordination, leading to a significant improvement of AB hydrolysis [57]. Furthermore, considering the lower abundance in the Earth's crust and the corresponding higher cost of Co compared with Ni, the $\text{Co}_{0.7}\text{Ni}_{0.3}\text{B-}h$ nanocatalyst possesses the optimal comprehensive performance. Therefore, the present molar ratio of Co: Ni (0.7:0.3) in the CoNiB-*h* system has been determined to be the most appropriate molar ratio for the hydrolysis of AB.

Figure 7a presents the catalytic decomposition kinetics profiles for hydrogen generation from the hydrolysis of AB at temperatures ranging from 298 to 313 K. As expected, the catalytic activities elevated with the increasing reaction temperature. The Arrhenius plot of ln k vs. 1/T for $\text{Co}_{0.7}\text{Ni}_{0.3}\text{B}$ -*h* is shown in Fig. 7b, from which the activation energy (E_a) is calculated (Eq. 2) to be 32.3 kJ mol⁻¹.

The recycle stability of a catalyst is vital in practical applications. As shown in Fig. 8, there is no apparent deactivation after four runs for the $Co_{0.7}Ni_{0.3}B$ -*h* catalyzed system, indicating that the $Co_{0.7}Ni_{0.3}B$ -*h* catalyst has a good stability for AB hydrolytic dehydrogenation reaction. Moreover, in this series of experiments, the usage of magnetic nanomaterials containing iron family elements (i.e., Fe, Ni, and Co) is advantageous to their recyclability in catalysis applications due to the ease of magnetic separation, especially in a liquid-phase reaction [58, 59].



Fig.8 Recycle test of the $\text{Co}_{0.7}\text{Ni}_{0.3}\text{B-}h$ nanocatalyst toward the hydrolysis of AB (0.16 M, 10 ml) at room temperature

4 Conclusions

Surfactant-free CoNiB NPs with different B contents have been facilely synthesized through two different reduction approaches. Compared to the ex-situ $\text{Co}_{0.7}\text{Ni}_{0.3}\text{B-}l$ catalyst that has a low B content, the in-situ $\text{Co}_{0.7}\text{Ni}_{0.3}\text{B-}h$ catalyst possesses higher B content and better dispersion, and it exhibits superior catalytic activity with a total TOF value of 30.9 min⁻¹ for hydrogen generation reaction from the hydrolysis of AB. This remarkably improved catalytic performance is attributed to the electron transfer between the incorporated B and the active metal sites, clean surface and good dispersion. Moreover, this convenient synthetic method represents a promising step towards developing other B incorporated metal catalysts for various applications.



Fig. 7 a Temperature effects on hydrogen generation rate catalyzed by $Co_{0.7}Ni_{0.3}B$ -h NPs from AB hydrolysis and b ln k vs. 1/T plot obtained from the data of Fig. 7a

Acknowledgements This work was supported by National Natural Science Foundation of China (51601018, 51608050, 51671035, 51605042); Jilin Province Science and Technology Development Project (20170520122JH, 20150520020JH); and Science and Technology Research Project of the Education Department of Jilin Province (JJKH20170549KJ, 2016327).

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