Bimetallic RuM (M=Co, Ni) Alloy NPs Supported on MIL-110(Al): Synergetic Catalysis in Hydrolytic Dehydrogenation of Ammonia Borane

Hong-hui Ning, Di Lu, Li-qun Zhou*, Meng-huan Chen, Yue Li, Gao-jian Zhou, Wei-wei Peng, Zheng Wang

Hubei Collaborative Innovation Center for Advanced Organic Chemical Materials, Ministry of Education Key Laboratory for the Synthesis and Application of Organic Functional Molecules, College of Chemistry and Chemical Engineering, Hubei University, Wuhan 430062, China

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By adjusting various Ru/M (M=Co, Ni) molar ratios, a series of highly dispersed bimetallic RuM alloy nanoparticles (NPs) anchored on MIL-110(Al) have been successfully prepared via a conventional impregnation-reduction method. And they are first used as heterogeneous catalysts for the dehydrogenation reaction of AB at room temperature. The results reveal that the as-prepared RuCo@MIL-110 and RuNi@MIL-110 exhibit the highest catalytic activities in different RuCo and RuNi molar ratios, respectively. It is worthy of note that the turnover frequency (TOF) values of RuCo@MIL-110 and RuNi@MIL-110 catalysts reached 488.1 and 417.1 mol H$_2$ min$^{-1}$ (mol Ru)$^{-1}$ and the activation energies ($E_a$) are 31.7 and 36.0 kJ/mol, respectively. The superior catalytic performance is attributed to the bimetallic synergistic action between Ru and M, uniform distribution of metal NPs as well as bi-functional effect between RuM alloy NPs and MIL-110. Moreover, these catalysts exhibit favorable stability after 5 consecutive cycles for the hydrolysis of AB.

Key words: RuCo@MIL-110, RuNi@MIL-110, Ammonia borane, Hydrogen production

I. INTRODUCTION

Metal-organic frameworks (MOFs) is a new emerging class of multiporous materials that consist of organic struts joined with inorganic nodes [1]. Due to the ultrahigh porosity and large surface area [2], together with chemical tunability and structural modifiability [3], the area of MOFs has become one of the fastest growing fields in chemistry [4], such as gas absorption and storage [5, 6], energy technologies [7], thin film devices [8], chemical sensors [9], and heterogeneous catalysis [10–12]. The tunable pores of MOFs can be employed to control the growth and hinder the aggregation of metal NPs in confined cavities, that markedly improved the catalytic performance and durability [13]. So far, many different kinds of metal NPs@MOFs catalysts have been studied, such as noble metal Pt@MIL-101 [14], non-noble metal Cu-MOF-74 [15], as well as composites, Ru-Ni@MOF-74(Ni) [16], CuCo@MIL-101 [17] and Pd/CoCeMIL-101 [18], etc.

On the other hand, the practical application of hydrogen energy was limited by safe transforming and efficient hydrogen storing. Finding suitable hydrogen storage materials is a great challenge towards a hydrogen-application society for eliminating current energy issues [19–21]. Ammonia borane (NH$_3$BH$_3$, AB) is attracting intense attention due to its higher hydrogen content, lower molecular weight and well-behaved solubility/stability in aqueous solutions under ambient conditions [22, 23], and becoming a non-toxicity convenient material for storing hydrogen. AB can release H$_2$ by thermolysis or solvolysis, but the most efficient method for the hydrolysis of AB is to seek high-efficient and low-cost catalyst. The hydrolysis reaction of AB can produce 3 mol of H$_2$ per mol of AB according to Eq.(1) [24, 25]:

$$\text{NH}_3\text{BH}_3 + 2\text{H}_2\text{O}_\text{Catalyst} \rightarrow \text{NH}_4\text{BO}_2 + 3\text{H}_2 \quad (1)$$

Up to now, a wide range of catalysts have been extensively applied for the hydrolytic dehydrogenation of AB, such as Ru/ND [26], AgPd@UIO-66-NH$_2$ [27], Ru-Rh@PVP [28], RuCo@MIL-96 [3] and Ni-Pt@CS [29], etc. To improve and control the rate of H$_2$ evolution from the hydrolysis of AB, we tried to focus on MIL-110(Al) and bimetallic RuCo and RuNi NPs. MIL-110(Al), as a new aluminum trimesate with formula Al$_8$(OH)$_{12}$(OH)$_3$(H$_2$O)$_3$[btc]$_3$nH$_2$O, has many merits such as honeycomb-like network structures, large theoretical specific surface area, high porosity, definite ranges of favorable stability, and ultra low density [30, 31], so it can be chosen as a support. Based on the above properties, RuCo and RuNi alloy NPs can be
well diffused into its pores or anchored on its surface, which is of great significance for reducing the agglomeration, controlling the growth of RuM (M=Co, Ni) NPs and further providing more active sites for dispersed metal NPs. Doping non-noble metals Co and Ni in noble metal Ru catalyst can not only reduce the cost of catalyst, but also improve the catalytic activity caused by the synergistic effects between noble metal and non-noble metals. What’s more, the existence of bi-functional effects between RuM alloy NPs and MIL-110 can enhance remarkably the catalytic activity and maintain good durability after several cycles. Until now, there is no reports about RuCo and RuNi NPs supported on MIL-110(Al) as heterogeneous catalysts applying for the H2 production from the hydrolysis of AB. Therefore, study on the synthesis and catalytic performances of RuM@MIL-110 (M=Co, Ni) catalysts is very important and challenging.

In the work, a series of bimetallic RuM@MIL-110 (M=Co, Ni) catalysts were fabricated and characterized by XRD, XPS, BET, TEM, FT-IR and ICP-AES. Different molar ratios of Ru to M were investigated to seek the optimal catalyst with satisfied catalytic performance and minimum amount of metal used. It is found that Ru1Co0@MIL-110 and Ru2Ni1@MIL-110 exhibit outstanding catalytic activities and superior cyclic stabilities for the AB hydrolysis reaction. Additionally, the activation energy (Ea) of catalytic hydrolysis reaction has been tested by changing the experimental temperature.

II. EXPERIMENTS

A. Chemicals and materials

Trimethyl 1,3,5-benzenetricarboxlyate (Me3btc), aluminum nitrate nonahydrate, sodium hydroxide, ruthenium chloride hydrate, cobalt nitrate hexahydrate, nickelous nitrate hexahydrate, dimethylformamide (DMF) and sodium borohydride were obtained from Sinopharm Chemical Reagent Co., Ltd, which were analytical reagent and used as received. The ammonia borane (AB) was purchased from Energy Chemical. Additionally, de-ionized water was employed in all experiments.

B. Preparation of MIL-110(Al)

The support material MIL-110(Al) were synthesized according to the previously reported method with slight modification [30]. Typically, 440 mg of Me3btc, 1312 mg of Al(NO3)3·9H2O, 2 mL of 4 mol/L NaOH, and 20 mL of de-ionized water were mixed in a 50 mL Teflon-liner autoclave and heated at 210 °C for 3 h. The white powder of MIL-110(Al) was collected by filtration. To get the empty pore phase MIL-110, the following steps were applied for removing the remaining Me3btc: the white product and appropriate amount of DMF were transferred to a autoclave and heated at 150 °C for 5 h. After filtration, the white precipitation MIL-110 was refluxed in a de-ioned water at 100 °C for 12 h and the purified products were dried in an vacuum oven for 12 h at 80 °C.

C. Synthesis of catalysts

For the synthesis of Ru1Co1@MIL-110 catalyst: Firstly, 50 mg of MIL-110 and 30 mL of de-ionized water were placed in a flask, and the mixture sonicated for 20 min to obtain a uniformly dispersed suspension. Then, 2.5 mL of RuCl3 solution (0.01 mol/L) and 2.5 mL of Co(NO3)2 aqueous solution (0.01 mol/L) were added into the flask with a pipette. The suspension solution was stirred by a magnetic force and continued for 6 h. Next, the resulting solution was reduced by 10 mL of NaBH4 (50 mg) aqueous solution and continuously stirred at room temperature for 3 h. After 3 h reduction, the black Ru1Co1@MIL-110 catalyst was assembled by filtration and dried overnight at 80 °C under vacuum. The Ru1Ni1@MIL-110 was also prepared by the same method only Ni(NO3)2 substituted for Co(NO3)2.

For the synthesis of Ru1Co0@MIL-110 (x=0.5, 2, 3) and Ru1Ni0@MIL-110 (y=0.5, 2, 3) catalysts were also fabricated in this work by the same process except that the amounts of Co and Ni were changed. Additionally, during the preparation of mono-metallic Ru@MIL-110, Co@MIL-110, Ni@MIL-110, pure RuCo and RuNi NPs catalysts, the theoretical addition of Ru3+, Co2+ and Ni2+ should be in good consistence with that of Ru1Co1@MIL-110 and Ru1Ni1@MIL-110. The typical fabrication of Co@MIL-110 catalyst described as the following: 50 mg of as-prepared MIL-110, 2.5 mL of 0.01 mol/L Co(NO3)2 and 30 mL of deionized water were mixed and sonicated, then reduced by 50 mg of NaBH4 with vigorous stirring. The preparation of RuCo NPs was also performed: 2.5 mL of 0.01 mol/L RuCl3, 2.5 mL of 0.01 mol/L Co(NO3)2 and 30 mL of water were mixed and sonicated for 20 min to get a well-dispersion solution. Then 10 mL 50 mg of NaBH4 was added to the above mixture and kept stirring for 3 h. The RuCo NPs were obtained by filtering, washing and drying.

D. Catalytic performance testing

To evaluate the catalytic performance of the as-prepared catalysts for the hydrolytic dehydrogenation of AB, 5 mg of catalysts were dispersed in 10 mL of deionized water kept in a double-necked round-bottom flask. The two necks of the flask were connected with a pressure-equalization funnel and a gas burette, re-
spectively. The gas burette was employed to monitor the volume change of H2 produced from the catalytic hydrolysis of AB and the pressure-equilization funnel was used to contain 10 mL of ammonia borane (18.5 mg, 0.6 mmol) solution. Once the piston of funnel was opened, the catalytic hydrolysis reaction of AB started immediately. At the same time, the volume of the released H2 was measured by the water displacement method every 30 s. The temperature of reaction solution was controlled at 25 °C through a water bath.

To further investigate the effect of temperature on catalytic activities, the hydrolytic reactions of Ru1Co@MIL-110 and Ru1Ni@MIL-110 catalysts were performed at different temperatures from 25 °C to 40 °C, respectively.

E. Analysis of durability

For durable recyclability research of the as-prepared Ru1Co@MIL-110 and Ru1Ni@MIL-110 catalysts, the catalytic hydrolysis reaction of AB was repeated 5 times by adding another 18.5 mg of AB into the solution after the previous catalytic reaction is over.

F. Catalyst characterization

PXRD measurement was performed on a Bruker D8-Advance X-ray diffractometer using Cu Kα radiation source (λ=0.154178 nm). The FT-IR spectra of the as-synthesized catalysts were recorded on a Nicolett (Madison, WI, USA) Impact 420 apparatus. The electronic states of the as-prepared Ru1Co@MIL-110 and Ru1Ni@MIL-110 catalysts were investigated by XPS (Thermo ESCALAB 250Xi). Specific surface area measurement was characterized with N2 adsorption-desorption isotherm obtained at 77 K using a Micromeritics ASAP 2020 instrument. TEM images were captured by a Tecnai G2F20 (FEI, Holland) transmission electron microscope (TEM). Elemental compositions of the Ru1Co@MIL-110 and Ru1Ni@MIL-110 catalysts were measured by ICP-AES using an IRIS Intrepid II XSP.

G. Evaluation of catalytic performances

Catalytic activities of RuCo@MIL-110 and RuNi@MIL-110 catalysts were performed in a double-necked round-bottom flask at room temperature. Herein, we adopt the state equation of ideal gas \( PV=nRT \) to calculate the actual content of H2 produced from the catalytic hydrolysis of AB. The atmospheric pressure of reaction is 101.325 kPa and the temperature is 298 K.

The actual loading of Ru in 5 mg RuM@MIL-110 (M=Co, Ni) catalysts was measured by the ICP-AES, the molar content of Ru can be calculated by the following equation (Eq.(2))

\[
 n_{(Ru)} = \frac{n_{(cat)}}{M_{(Ru)}} \tag{2}
\]

According to Eq.(3), the turnover frequency (TOF) values of as-synthesized Ru1Co@MIL-110 and Ru1Ni@MIL-110 catalysts are 488.1 and 417.1 mol H2 min\(^{-1}\) (mol Ru)\(^{-1}\), respectively.

\[
 \text{TOF} = \frac{n_{(H2)}}{n_{(Ru)} t_{(min)}} \tag{3}
\]

III. RESULTS AND DISCUSSION

The XRD patterns of the as-obtained MIL-110, Ru@MIL-110, Co@MIL-110, Ni@MIL-110, Ru1Co@MIL-110, Ru1Ni@MIL-110, as well as Ru1Co@MIL-110 and Ru1Ni@MIL-110 after the fifth run are displayed in FIG. 1 (A) and (B). The XRD pattern of the as-prepared MIL-110 are matched well with previously reported results [32], demonstrating that the pure MIL-110 was prepared. In FIG. 1 (A) and (B), all of the diffraction peaks of Ru@MIL-110, M@MIL-110, Ru1M@MIL-110 (M=Co, Ni) and Ru1M@MIL-110 after the fifth run samples are in good agreement with those of the parent MIL-110, suggesting that the crystalline structure of MIL-110 has unchanged during the fabrication and catalytic process of the catalysts. However, the intensities of four groups of diffraction peaks of the samples decreased obviously in contrast to that of MIL-110. The plausible explanation for this phenomenon is the variation in the charge distribution and electrostatic fields caused by the existence of RuCo and RuNi NPs on the surface as well as interaction of their electrophilic surface with MIL-110 skeleton atoms [33]. Notably, no striking diffraction peak corresponding to metal Ru, Co and Ni species can be detected because of the low metal loading or the amorphous phases of Ru, Co and Ni NPs [34]. Additionally, the XRD peaks of Ru at about 44.1° in the catalyst Ru@MIL-110 can be observed in FIG. 1(C), but the diffraction peaks of Ru from Ru1Co@MIL-110 and Ru1Ni@MIL-110 shift slightly to higher 2θ values from 44.1° to 44.8° and 44.7°, respectively, illustrating that the addition of small Co or Ni atoms into Ru lattice leads to a lattice contraction [35]. The above results confirm the formation of the RuCo and RuNi alloys [36], thus the positive synergistic action between Ru and M (M=Co, Ni) could be formed and significantly improve the catalytic performance for the catalytic hydrolysis of AB.

The XPS was employed to analysis the composition and electronic states of Ru1Co@MIL-110 and Ru1Ni@MIL-110 catalysts. The peaks of C 1s and
FIG. 1 Powder X-ray diffraction patterns of (A) Ru$_1$Co$_1$@MIL-110, (B) Ru$_1$Ni$_1$@MIL-110 and (C) the magnified Ru: (a) MIL-110, (b) Ru@MIL-110, (c) M@MIL-110 (M=Co, Ni), (d) Ru$_1$M$_1$@MIL-110, (e) Ru$_1$M$_1$@MIL-110 after the fifth run.

FIG. 2 XPS spectra of Ru$_1$Co$_1$@MIL-110 and Ru$_1$Ni$_1$@MIL-110: (a) the survey scan, (b) Ru 3p, (c) Co 2p, (d) Ni 2p.

Ru 3d appear at 285 eV and overlap intensively, making it much difficult to analyze ruthenium properly in this area (FIG. 2(a)) [37]. From FIG. 2(b), it can be seen that the binding energies at 462.0 and 485.1 eV can be attributed to the Ru(0) 3p$_{3/2}$ and Ru(0) 3p$_{1/2}$, respectively [38]. In FIG. 2(c), the binding energies of Co 2p at 781.5 and 786.2 eV are ascribed to the Co 2p$_{3/2}$ peaks of Co$^{2+}$, the peaks centered at 797.5 and 803.1 eV belong to the Co 2p$_{3/2}$ peaks of Co$^{2+}$ [39, 10]. The weak peaks at 778.1 and 793.0 eV are assigned to Co(0) 2p$_{3/2}$ and Co(0) 2p$_{1/2}$ [17, 40], respectively. FIG. 2(d) reveals that the binding energies of Ni 2p at 856.5 and 874.5 eV can be ascribed to Ni 2p$_{3/2}$ and Ni 2p$_{1/2}$ peaks of Ni(0), respectively. And
the two peaks located at 862.4 and 879.6 eV can be attributed to Ni 2p$_{3/2}$ and Ni 2p$_{1/2}$ of Ni$^{2+}$, respectively, such as NiO and Ni(OH)$_2$ [41, 27]. The above results confirm that Ru$^{3+}$, Co$^{2+}$ and Ni$^{2+}$ have been reduced to Ru, Co and Ni, but part of Co and Ni may be oxidized during the preparation of RuCo@MIL-110 and RuNi@MIL-110. Based on the electrode potential ($E^o$(Ru$^{3+}$/Ru)=$+0.40$ eV; $E^o$(Co$^{2+}$/Co)=$-0.28$ eV; $E^o$(Ni$^{2+}$/Ni)=0.25 eV) [42, 43], Ru$^{3+}$ with a higher potential is first reduced to Ru by NaBH$_4$, then produce active intermediate Ru-H species, which may facilitate the conversion of Co$^{2+}$ to Co and Ni$^{2+}$ to Ni [44].

The N$_2$ sorption isotherms of MIL-110, Ru$_1$Co$_1$@MIL-110, and Ru$_1$Ni$_1$@MIL-110 are shown in FIG. 3. The BET surface area of the MIL-110 was 410.2 m$^2$/g [32, 45], further verifying the porous structure of MIL-110 support. However, the special area of MIL-110 dramatically declined to 127.4 and 112.2 m$^2$/g after RuCo and RuNi alloy NPs were loaded, respectively. The above phenomena illustrate that the cavities of MIL-110 were either occupied or blocked by the well dispersed RuM (M=Co, Ni) alloy NPs.

The morphologies of MIL-110 supported Ru, RuCo and RuNi NPs were further performed by HRTEM. FIG. 4(a) shows that part of Ru NPs aggregated on the surface of MIL-110, and the average particle size of Ru NPs was (2.7±0.3) nm (FIG. 4(e)). FIG. 4(b) indicates that RuCo NPs are well dispersed on the surface of the supported material MIL-110. Notably, no apparent aggregation of RuCo NPs is observed. From FIG. 4(c), RuNi NPs on the surface of MIL-110 also exhibit good distribution, but the dispersed degree of RuNi NPs is slightly inferior than that of RuCo NPs. FIG. 4(d) suggests that the morphologies of Ru$_1$Co$_1$@MIL-110 after the fifth run has almost unchanged, and RuCo alloy NPs well dispersed on the surface of MIL-110 similar to Ru$_1$Co$_1$@MIL-110. The particle size of RuCo alloy NPs in Ru$_1$Co$_1$@MIL-110 after the fifth run is (2.2±0.3) nm, very close to that of Ru$_1$Co$_1$@MIL-110 (FIG. 4(h)).

In view of the above results, the Ru$_1$Co$_1$@MIL-110 catalyst can maintain a good morphology, similar properties also exist in the Ru$_1$Ni$_1$@MIL-110 catalyst. As shown in FIG. 4 (f) and (g), the average particle diameters of RuCo and RuNi alloy NPs supported on MIL-110 were about (2.4±0.3) and (2.6±0.3) nm, respectively, slightly lower than that of Ru NPs.

It is well-known that the metallic particle size and distribution play a critical role in heterogeneous catalytic field. Hence, the catalytic activity of Ru$_1$Co$_1$@MIL-110 slightly higher than that of the Ru$_1$Ni$_1$@MIL-110 catalyst under the same conditions, because the Ru$_1$Co$_1$@MIL-110 has the merits of relatively small particle size, uniform distribution and less aggregation. As previous reported, the diameter of pore of the support MIL-110 was about 1.6 nm [31], so that the smaller RuCo and RuNi alloy NPs could be easily embedded into the pores. On the contrary, the larger particle size could be immobilized on the surface. The uniformly distributed and well encapsulated RuM alloy NPs in the Ru$_1$M$_1$@MIL-110 (M=Co, Ni) reasonably explained the excellent catalytic behaviors than that of the Ru@MIL-110.

Moreover, the contents of Ru, Co and Ni in the RuCo@MIL-110 and RuNi@MIL-110 catalysts were measured by ICP-AES and recorded in Table I and Table II. Table I shows that the actual weight ratio of Ru:Co (1.0, 1.0:0.48, 1.0:0.97, 1.1:0.91, 1.2:7.63) are well matched with the theoretical ratios in the Ru$_x$Co$_{1-x}$@MIL-110 (x=0, 0.5, 1, 2, 3) catalysts, respectively. Nevertheless, it is significant that the content of Co is lower than its theoretical addition in all samples, which can be explained by the difference of reduction potentials as mentioned above. Similarly, in Table II,

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FIG. 4 TEM images of (a) as-prepared Ru@MIL-110, (b) Ru$_1$Co$_1$@MIL-110, (c) Ru$_1$Ni$_1$@MIL-110, (d) Ru$_1$Co$_1$@MIL-110 after the fifth run. Particle size distributions of (e) Ru@MIL-110, (f) Ru$_1$Co$_1$@MIL-110, (g) Ru$_1$Ni$_1$@MIL-110, (h) Ru$_1$Co$_1$@MIL-110 after the fifth run.

The actual weight ratio of Ru:Ni (1:0.49, 1:0.98, 1:1.92, 1:2.87) is very close to the precursor ratios in the Ru$_1$Ni$_y$@MIL-110 ($y$=0, 0.5, 1, 2, 3) catalysts, respectively.

Contrasting Table I with Table II, it can be clearly observed that the actual loading of RuNi is slightly higher than that of RuCo, which may be related to the higher electrode potential of Ni$^{2+}$/Ni. However, the catalytic performance of Ru$_1$Co$_1$@MIL-110 is slightly higher than that of Ru$_1$Ni$_1$@MIL-110 toward hydrolysis of AB. The abnormal phenomenon may concern the difference of the synergistic effects. It is well-known that the synergetic effects between alloy nanoparticles mainly involve geometric effects and electronic effects. In the RuM crystal structures, Ru and Co belong to hexagonal crystal, with the A$_3$-type structure, while
Ni is the face-centered cubic crystal with the $A_1$-type structure, shown in FIG. 5. When RuCo alloy NPs form, Co will replace part of Ru in the Ru lattices and the crystal structure maintains well. Therefore, there exist strong geometric effects between Ru and Co. While RuNi alloy NPs forms, the doping of Ni may cause a few lattice distortion of Ru, leading to a inferior geometric effects than that of RuCo alloy. Furthermore, there exist intense electronic effects between Ru and M in RuM alloy NPs due to the electronegativities difference of Ru (2.2), Co (1.88) and Ni (1.91), and the greater the electronegative difference between the two elements, the stronger the electronic effect. As a result of the above, Ru$_1$Co$_x$@MIL-110 and Ru$_1$Ni$_y$@MIL-110 have similar catalytic properties, but the former has a slightly higher activity than the latter for the H$_2$ production from AB.

FIG. 6 shows the FT-IR spectra of MIL-110, Ru$_1$Co$_x$@MIL-110 and Ru$_1$Ni$_y$@MIL-110 catalysts. In FIG. 6(A), compared with MIL-110, the location and intensity of peaks of Ru$_1$Co$_x$@MIL-110 and Ru$_1$Co$_x$@MIL-110 after the fifth run show no significant changes, being consistent with the results of XRD. Similarly, FIG. 6(B) indicates that the FT-IR peaks of initial Ru$_1$Ni$_y$@MIL-110 and Ru$_1$Ni$_y$@MIL-110 after fifth cycles are all in accord with those of MIL-110, illustrating that the structural integrity of MIL-110 was maintained well in the process of fabrication and catalytic cycles, and providing a good foundation for RuCo and RuNi alloy NPs effectively supported on the framework of MIL-110 after multiple catalytic runs.

To evaluate the catalytic performances, the as-synthesized Ru$_1$Co$_x$@MIL-110 and Ru$_1$Ni$_y$@MIL-110 samples have been applied for the catalytic hydrolysis of AB at room temperature. FIG. 7 shows that the two bimetallic systems Ru$_1$Co$_x$@MIL-110 and Ru$_1$Ni$_y$@MIL-110 exhibit the highest catalytic performance. Furthermore, it is obvious that the bimetallic Ru$_1$Co$_x$@MIL-110 shows different catalytic properties with the changing of the molar ratio of Ru to Co in FIG. 7(a). The rate of hydrogen generation ascended first and then descended from 1:0.5, 1:1, 1:2 to 1:3 of Ru to Co. Analogously, FIG. 7(b) illustrates that the catalytic behaviors of the Ru$_1$Ni$_y$@MIL-110 catalysts also exhibit identical trend with the variation of $y$ ($y=0.5, 1, 2, 3$). It can be explained by the catalytic mechanism of the Ru$_1$Co$_x$@MIL-110 and Ru$_1$Ni$_y$@MIL-110 in the H$_2$ generation from the hydrolysis of AB. It is generally known that the activation process mainly takes place on the surface area of the metal catalyst [46]. The possible mechanism involves the following two steps: the first step is formation of an activated transient metal-H between AB and the surface of RuCo and RuNi alloy NPs, which is the rate-determining step for the catalytic reaction. The second step is the H$_2$ released after water attacking the metal-H species [47]. To a certain extent, the dispersed degree of RuCo and RuNi alloy NPs on the support MIL-110 with the increasing loading of Co and Ni can enhance the contact area between AB and metal NPs, and increase the number of active sites with the activated transient metal-H. However, when the excessive Co and Ni coverage on the surfaces of Ru, the active sites of Ru will be reduced [48], or there exist too strongly bindings between reactant AB and the surface of Ru, that will cause all available surface sites to be occupied and the catalyst to be poisoned [49]. Based on the above point, it is safe to infer that the increasing contact area between AB and metal NPs, the activated transient metal-H and the synergistic catalysis effects of alloying Ru with Co and Ni in the RuCo@MIL-110
FIG. 7 Hydrogen generation from the hydrolysis of AB catalyzed by (a) RuCo@MIL-110 and (b) RuNi@MIL-110 (5 mg catalysts, 18.5 mg AB at 25 °C) and (c, d) corresponding hydrogen generation rate versus M (M=Co, Ni) molar ratio.

and RuNi@MIL-110 catalysts account for the increasing catalytic performance with the rising molar ratio of Ru/Co and Ru/Ni from 1:0 to 1:1. However, the catalytic behavior is decreasing when the molar ratio of Ru:M is larger than 1:1.

For comparison, the monometallic Ru@MIL-110, Co@MIL-110, Ni@MIL-110, and activated MIL-110 catalysts are also synthesized and their catalytic behaviors for the catalytic hydrolysis reaction of AB are studied. It is noteworthy that no obvious H₂ production is

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detected for Co@MIL-110, Ni@MIL-110 and the matrix MIL-110 from FIG. 8(a), illustrating that these samples have negligible catalytic performances for the hydrolysis of AB. Furthermore, the catalytic activities of bimetallic RuCo@MIL-110 and RuNi@MIL-110 outperform that of monometallic Ru@MIL-110 with the same amount of Ru. In FIG. 8(b), when the contents of Ru, Co and Ni are consistent with that in RuCo@MIL-110 and RuNi@MIL-110, the catalytic activities of the mixtures of monometallic counterparts Ru@MIL-110 and RuCo@MIL-110 and RuNi@MIL-110 catalysts are significantly lower than that of the RuCo@MIL-110 and RuNi@MIL-110 catalysts, respectively, further confirming that the strong synergistic actions between Ru and Co, Ni NPs plays a decisive part in improving the catalytic performance. Similar synergistic effects were discovered in the previously reported literatures, such as RuCo/Ti3C2X2 [50], RuNi/TiO2 [51]. Additionally, the catalytic activities of RuCo@MIL-110 and RuNi@MIL-110 outperform the pure RuCo and RuNi NPs, indicating that the bi-functional effects between RuM (M=Co, Ni) alloy NPs and the host of MIL-110 can enhance the H2 releasing rate, and offer a stable structure for RuCo or RuNi alloy NPs to immobilize on its surface and cage. FIG. 8(c) shows that there exist similar catalytic performances between RuCo@MIL-110 and RuNi@MIL-110 as well as RuCo and RuNi alloy NPs, and the former is slightly higher than the latter, which are well in line with the analysis of the FIG. 5.

The activation energies (Ea) of AB hydrolysis reaction catalyzed by RuCo@MIL-110 and RuNi@MIL-110 were tested in the temperature range of 25–40 °C. FIG. 9(a) shows that the H2 evolution rate increases with the elevating reaction temperature, and the rate constant k at different temperatures is calculated based on the slope of the linear portion of each plot. In FIG. 9(b), the Arrhenius plot shows that the Ea values of RuCo@MIL-110 and RuNi@MIL-110 catalysts are 31.7 and 36.0 kJ/mol, respectively, which are lower than the activation energies reported for most of Ru-based catalysts (see Table III).

The cycle stability is of significance for the practical application of catalysts. We studied the reusability of RuCo@MIL-110 and RuNi@MIL-110 catalysts for the hydrolysis reaction of AB. In FIG. 10(a), the RuCo@MIL-110 still exhibits satisfied catalytic activities even after 5 consecutive cycles. Compared to the first catalytic performance of RuCo@MIL-110 catalyst, the retained percent catalytic activities through five cycles are 100%, 94.1%, 88.2%, 83.2%, and 79.0%, respectively. It is noteworthy mentioned that only 5 mg of the catalyst involved in the catalytic reaction exhibit favorable catalytic activity. Similarly, FIG. 10(b) reveals the RuNi@MIL-110 catalyst also has superior catalytic behaviors after the reuse, and the retained percent catalytic activities through one to five cycles are 100%, 93.3%, 88.3%, 84.4% and 76.0%, respectively. Table IV shows that the metal leaching of RuCo@MIL-110 catalyst after five catalytic cycles were measured to be 3.11%, 4.96%, 6.85%, 8.74% and 10.62%, respectively. Similarly, from Table V, the

<table>
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<th>Catalyst</th>
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<th>TOF*/(mol H2 min⁻¹(mol Ru)⁻¹)</th>
<th>Ea/(kJ/mol)</th>
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<td>417.1</td>
<td>36.0</td>
<td>This study</td>
</tr>
<tr>
<td>Ru@Ni/graphene</td>
<td>0.004</td>
<td>339.5</td>
<td>36.59</td>
<td>[42]</td>
</tr>
<tr>
<td>Ru@g-C3N4</td>
<td>0.0012</td>
<td>313.0</td>
<td>37.4</td>
<td>[54]</td>
</tr>
<tr>
<td>RuCo@MIL-96</td>
<td>0.0017</td>
<td>320.7</td>
<td>36.0</td>
<td>[3]</td>
</tr>
<tr>
<td>RuCuNi/CNTs</td>
<td>0.0015</td>
<td>311.15</td>
<td>36.67</td>
<td>[38]</td>
</tr>
<tr>
<td>Ru/MCM-41</td>
<td>0.0055</td>
<td>288</td>
<td>41.6</td>
<td>[55]</td>
</tr>
<tr>
<td>Ru@MIL-53(Al)</td>
<td>0.004</td>
<td>266.9</td>
<td>33.7</td>
<td>[56]</td>
</tr>
<tr>
<td>Ru@MIL-53(Cr)</td>
<td>0.004</td>
<td>260.8</td>
<td>28.9</td>
<td></td>
</tr>
<tr>
<td>Ru/nanodiamond</td>
<td>0.003</td>
<td>229.0</td>
<td>50.7</td>
<td></td>
</tr>
<tr>
<td>Ru@SiO3</td>
<td>0.0025</td>
<td>200</td>
<td>38.2</td>
<td>[24]</td>
</tr>
<tr>
<td>Ru(0)/SiO2-CoFeO4</td>
<td>0.00194</td>
<td>172</td>
<td>45.6</td>
<td>[57]</td>
</tr>
<tr>
<td>Ru/graphene</td>
<td>0.01</td>
<td>100</td>
<td>11.7</td>
<td>[58]</td>
</tr>
<tr>
<td>RuCo/γ-Al2O3</td>
<td>0.0391</td>
<td>32.9</td>
<td>47.7</td>
<td>[59]</td>
</tr>
</tbody>
</table>

TOF values were taken directly from the related articles if they were reported. If not, the initial TOF values were calculated from the corresponding hydrogen generation versus time graphs presented in the article.

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metal leaching of Ru$_1$Ni$_1$@MIL-110 catalyst through five cycles were determined to be 3.25%, 4.95%, 6.63%, 8.28% and 9.93%, respectively. The high durability of the Ru$_1$Co$_1$@MIL-110 and Ru$_1$Ni$_1$@MIL-110 catalysts should be attributed to the fact that the structural integrity of MIL-110 was maintained well and the superfine RuM alloy NPs still favorably anchored on MIL-110 after five cycles. To the catalytic performance decreased after five cycles, the main reason might be caused by the metal leaching of Ru, Co and Ni. Meanwhile, the increased viscosity of the reaction solution and deactivation action of the increasing metaborate concentration should be taken into consideration, because they can exert negatively influence for the catalytic reaction [60].

IV. CONCLUSION

In summary, MIL-110 supported RuCo and RuNi alloy NPs have been successfully prepared by a facile impregnation-reduction method and applied for the AB hydrolysis reaction. Remarkably, the obtained Ru$_1$Co$_1$@MIL-110 and Ru$_1$Ni$_1$@MIL-110 exhibit superior catalytic performances with turn over frequency (TOF) value of 488.1 and 417.1 mol H$_2$ min$^{-1}$ (mol Ru)$^{-1}$ and the activation energies ($E_a$) were tested to be 31.7 and 36.0 kJ/mol, respectively. The promising catalysts benefit from the strong bimetallic synergistic actions, uniform distribution of NPs on the surface of MIL-110 as well as bi-functional effects between RuM alloy NPs and MIL-110. Additionally, the Ru$_1$Co$_1$@MIL-110 and Ru$_1$Ni$_1$@MIL-110 catalysts possess satisfied durabilities, retaining 79% and 76% of their initial activity after 5 cycles, respectively. This is the first example for RuCo and RuNi NPs immobi-

<table>
<thead>
<tr>
<th>TABLE IV</th>
<th>The metal leaching of Ru$_1$Co$_1$@MIL-110 (5 mg) in the subsequent runs of the hydrolysis of AB.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run</td>
<td>Ru/mg</td>
</tr>
<tr>
<td>1</td>
<td>0.0034</td>
</tr>
<tr>
<td>2</td>
<td>0.0050</td>
</tr>
<tr>
<td>3</td>
<td>0.0066</td>
</tr>
<tr>
<td>4</td>
<td>0.0082</td>
</tr>
<tr>
<td>5</td>
<td>0.0099</td>
</tr>
</tbody>
</table>
TABLE V The metal leaching of Ru₄Ni₈@MIL-110 (5 mg) in the subsequent runs of the hydrolysis of AB.

<table>
<thead>
<tr>
<th>Run</th>
<th>Ru/mg</th>
<th>Ni/mg</th>
<th>Metal/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0034</td>
<td>0.0025</td>
<td>3.25</td>
</tr>
<tr>
<td>2</td>
<td>0.0053</td>
<td>0.0036</td>
<td>4.95</td>
</tr>
<tr>
<td>3</td>
<td>0.0073</td>
<td>0.0046</td>
<td>6.63</td>
</tr>
<tr>
<td>4</td>
<td>0.0093</td>
<td>0.0056</td>
<td>8.28</td>
</tr>
<tr>
<td>5</td>
<td>0.0113</td>
<td>0.0065</td>
<td>9.93</td>
</tr>
</tbody>
</table>

lized on MIL-110(Al) and employed for the hydrolysis of AB. Therefore, facile preparation and outstanding catalytic behaviors suggest that the RuCo@MIL-110 and RuNi@MIL-110 catalysts may promote the practical applications of AB as promising hydrogen storage materials.

V. ACKNOWLEDGMENTS

This work was supported by the Natural Science Fund for Creative Research Groups of Hubei Province (No.2014CFA015), Hubei Province Education Office Key Laboratory (No.2016-KL-007) of China. This work was also supported by the Hubei College Students’ Innovation Training Program of China (No.201410512024 and No.201510512030).

