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## Fabrication and characterization of a novel nanoporous Co–Ni–W–B catalyst for rapid hydrogen generation†

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A highly active nanoporous Co–Ni–W–B alloy has been prepared using chemical reduction in an ethanol solution and tested as a novel catalyst for hydrolysis of ammonia borane. Compared with the alloy prepared in an aqueous solution, the as-prepared alloy shows a much higher surface area and hydrogen generation rate.

Hydrogen has been considered as a promising energy carrier due to its high efficiency and near zero emissions. However, developing a safe as well as an efficient method to store and produce hydrogen is still a challenge. With a high hydrogen capacity of 19.6 wt%, good stability and being non-toxic, ammonia borane (AB,  $\text{NH}_3\text{BH}_3$ ) is one of leading candidates for a hydrogen storage medium.<sup>1</sup> Typically, hydrogen stored in AB can be released by thermal dehydrogenation and hydrolysis. Comparing to the thermal dehydrogenation, the hydrolysis is more attractive because it can be carried out at room temperature and produce  $\text{H}_2$  without generating other unwanted byproducts.<sup>2,3</sup> Since AB has good stability in aqueous solution under room temperature, catalysts are often required to accelerate the hydrolysis reaction by lowering the kinetic barrier in a tunable manner.<sup>4</sup>

Various catalysts have been tested for AB hydrolysis,<sup>5–7</sup> among which noble metal such as Pt-based alloys exhibit the high catalytic activities.<sup>8–10</sup> However, the high cost and low abundance of noble metal limit their real-to-life practical applications. Therefore, it is of great interest to develop high performance and low cost catalysts. The catalysts based on transition metals, such as Co or Ni, are generally used to accelerate the hydrolysis reaction of AB due to their exceptional catalytic activity and low cost.<sup>4</sup> It has been demonstrated that

these catalysts show comparable catalytic activities to the noble metals.<sup>11,12</sup> However, the stability, surface oxidation and agglomeration of catalyst particles restrict their applications in the hydrogen generation reactors. Supporting the Co or Ni based catalyst on other substrates or introducing atomic barrier using transition metals, such as W, Cr, Cu, Mo, have been regarded as effective ways to improve the stabilities and dispersions of the active phases.<sup>13–16</sup> This is important, as the catalytic characteristics of these catalysts are strongly depending on their sizes, shapes, porosity, and preparation methods.<sup>13</sup>

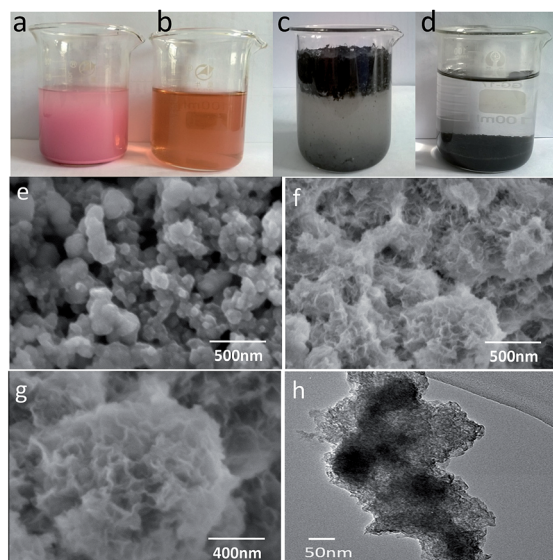
Nanoporous catalysts are currently under intensive investigations in the catalysis community due to their exceptional catalytic activities and selective natures when compared to the corresponding bulk counterpart.<sup>8,12</sup> The nanoporous catalysts have advantage of large surface-to-volume atomic ratios, sizes and shape dependent properties, and high concentration of low coordinated active surface sites, which increase the contact area with the reactants efficiently.<sup>10</sup> In the present study, a novel method of using corresponding metal salts suspended in ethanol solution is proposed to prepare a nanoporous Co–Ni–W–B catalyst. The Co–Ni–W–B catalyst formed exhibit superior catalytic activity when compared to the ones prepared from aqueous solution, due to its high surface area. The synthesized Co–Ni–W–B catalysts have been tested for understanding of their hydrogen generation abilities in AB solutions.

The preparation of Co–Ni–W–B alloy has been achieved using chemical reduction in ethanol solution. The metal salts such as  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  and  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  have limited solubility in ethanol solution and form suspension as shown in Fig. 1a and b. After adding  $\text{NaBH}_4$  solution into the suspension, the reduction occurs immediately. The interesting observation as shown in Fig. 1c and d is that reduced black precipitates float on top in the ethanol solution, while precipitates from same reaction move down to the bottom when aqueous solution used as the reaction medium. This indicates that the two precipitates have different density therefore structures.

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**Fig. 1** Photos (a) metal salts in ethanol; (b) metal salts in aqueous; (c) Co-Ni-W-B prepared in ethanol; (d) Co-Ni-W-B prepared in aqueous; SEM images of (e) Co-Ni-W-B prepared in aqueous, (f and g) Co-Ni-W-B prepared in ethanol; (h) TEM image of Co-Ni-W-B prepared in ethanol solution.

The SEM image in Fig. 1e shows that the Co-Ni-W-B powder prepared in aqueous is mainly composed of irregular aggregated particles with sizes in the range from 50 to 100 nm. Due to the exothermic nature of the reduction reaction and high surface energy involved, these particles are mostly formed in agglomerated state with low specific surface area.<sup>12</sup> In comparison, the Co-Ni-W-B prepared in ethanol presents nanoporous flower-like morphology composed of interconnected nanosheets. The TEM images also confirmed that the formation of nanosheet structures in the nanoporous structure as shown in Fig. 1h. Presumably, due to the low solubility of the metal salts in ethanol solution, the reaction rate is limited during the initial stage. After the dropwise addition of 20 mL of NaBH<sub>4</sub> solution, the mixture reacts vigorously and release large amount of hydrogen gas. The hydrogen gas pushes the particle up. In this process, the nanoporous structure is formed and hydrogen gas is confined in the pore, which enable the precipitation floating on the surface of the solution. However, due to the good solubility of metal salts in the aqueous solution, the reduced particles aggregate and sink in the water. The speculation is that the use of ethanol as the solvent leads to the formation of porous morphology, which could be due to the change in the nucleation and growth of the catalyst species during the synthesis. More investigations are required in the future to interpret the morphological formation mechanism.

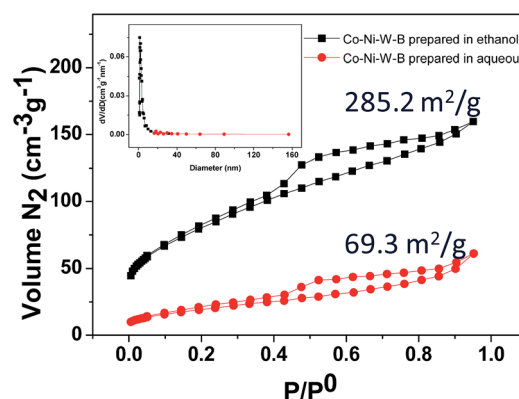
Energy dispersive X-ray (EDX) analysis indicates that the nanoparticles prepared from ethanol solution consist elements of Co, Ni, W and O (Fig. S2, ESI†). The observation of O element is possibly originated from sample preparation and washing in air.<sup>17</sup> The composition of the nanoporous catalyst has determined by using ICP-AES measurement to be 63.52 wt% Co, 19.94 wt% Ni, 9.36 wt% W, 7.44 wt% B, corresponding to a formula of Co<sub>21</sub>Ni<sub>7</sub>W<sub>1</sub>B<sub>13</sub>.

Nitrogen adsorption-desorption isotherms of the Co-Ni-W-B catalysts prepared in ethanol and aqueous are presented in Fig. 2. The inset of the figure shows the pore size distributions calculated using Barrett-Joyner-Halenda (BJH) method. The isotherm shows a typical IUPAC type pattern with inflection of N<sub>2</sub> adsorbed at  $P/P_0$  about 0.40, indicating the presence of mesopores.<sup>18</sup> The nanoporous Co-Ni-W-B has a large Brunauer-Emmett-Teller (BET) surface area of 285.2 m<sup>2</sup> g<sup>-1</sup> and the average pore diameter is 2.5 nm.

In comparison, Co-Ni-W-B alloy prepared in aqueous displays a BET surface area of 69.3 m<sup>2</sup> g<sup>-1</sup>. The specific surface areas (SSA) of Co-Ni-W-B prepared in ethanol is about 4 times higher than that of Co-Ni-W-B prepared in aqueous, which is due to the formation of the mesoporous structure in the Co-Ni-W-B flowers. Thus, it is expected that the porous Co-Ni-W-B provides a higher rate of H<sub>2</sub> generation in AB solution.<sup>10</sup>

The X-ray diffraction (XRD) patterns of the Co-Ni-W-B prepared by using chemical reduction method display broad peak around 30–50° for the Co-Ni-W-B sample prepared in aqueous solution, indicating their amorphous structures (Fig. S3, ESI†). In contrast, sharper diffraction peaks are observed for the Co-Ni-W-B prepared in ethanol, which indicate that this type of Co-Ni-W-B prefers to crystallize. It is probably because that using ethanol as the solvent enables the transformation of Co-Ni-W-B from amorphous phase to its crystalline phase, but the mechanism is currently unclear. However, it has been considered that the amorphous structure may enhance the catalytic activity due to their unique short-range ordering but long-range disordering structure, surface coordinating unsaturated sites and the lack of crystal defects.<sup>18</sup>

The catalytic performance of the as-prepared catalyst was determined by measuring the HG rate of AB hydrolysis (1 wt% solution, 10 mL) at 30 °C. The amount of catalysts (0.01 g) loading was kept same for all the catalyst powders. Fig. 3 shows the volumes of hydrogen generated by the Co-Ni-W-B catalysts prepared from using different solutions. Hydrogen is instantaneously produced as soon as the AB soon come in contact with catalysts without any induction time and reach the 100% of the theoretical hydrogen yield for both catalysts. The required



**Fig. 2** N<sub>2</sub> adsorption and desorption isotherm and pore distribution (inset) of Co-Ni-W-B prepared in aqueous and Co-Ni-W-B prepared in ethanol.

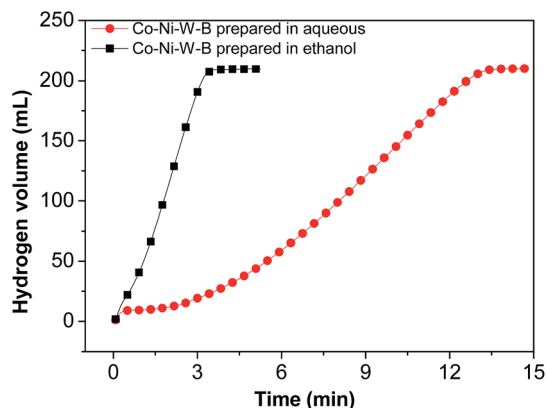


Fig. 3 Hydrogen generation of AB using Co-Ni-W-B catalysts prepared in aqueous solution and in ethanol, respectively (batch system, 30 °C, 1.0 wt% AB, 0.01 g catalyst).

reaction time to complete the reaction was approximately 2.5 min in the presence of nanoporous Co-Ni-W-B prepared in ethanol, which was much shorter than the 13 min from using Co-Ni-W-B prepared in aqueous. The HG rates ( $r$ ) were calculated by using equation:  $r = (V/t)/m$ , where  $V$  is the generated hydrogen volume (mL),  $m$  is the amount of catalyst (g).<sup>13</sup> From the slopes of the fitting lines that were obtained from the  $V$ - $t$  curves, the hydrogen generation (HG) rates of Co-Ni-W-B prepared in respective aqueous and ethanol solutions were 1430 and 6360 mL min<sup>-1</sup> g<sup>-1</sup> catalyst. The nanoporous Co-Ni-W-B catalyst from preparation in ethanol shows about 4.5 times higher HG rate than that of the ones prepared in aqueous. The obtained HG rate value is significantly higher than other known catalysts, such as Pd nanoparticles supported on MIL-101 (1008 mL min<sup>-1</sup> g<sup>-1</sup>),<sup>8</sup> *in situ* synthesized Fe nanoparticles (1519 mL min<sup>-1</sup> g<sup>-1</sup>),<sup>19</sup> Co-B supported on SBA-15 (1900 mL min<sup>-1</sup> g<sup>-1</sup>),<sup>12</sup> Co-P deposited on TiO<sub>2</sub> (2002 mL min<sup>-1</sup> g<sup>-1</sup>),<sup>20</sup> Co-W-B-P supported on Ni foam (4000 mL min<sup>-1</sup> g<sup>-1</sup>)<sup>13</sup> and *in situ* synthesized Fe<sub>0.5</sub>Ni<sub>0.5</sub> (5372 mL min<sup>-1</sup> g<sup>-1</sup>).<sup>21</sup> These results demonstrate that nanoporous Co-Ni-W-B is a highly active catalyst for AB hydrolysis.

For comparison, the ternary Co-Ni-B, Co-W-B, Ni-W-B and binary Co-B, Ni-B were also prepared in ethanol solution with same chemical reduction method. It can be seen that the nanoporous Co-Ni-W-B shows highest catalytic activity when compared to the same amount of Co-B, Ni-B, Co-Ni-B, Co-W-B, Ni-W-B catalyst powders (0.01 g) (Fig. S4, ESI†). The HG rates acquired with using these catalysts decrease in following order: Co-Ni-W-B > Co-W-B > Co-Ni-B > Ni-W-B > Co-B > Ni-B. This could be attributed to the introduction of transition metals, which are known to effectively improve the catalytic activity for hydrolysis of borohydride.<sup>3</sup>

The effect of AB concentration on the hydrogen generation rate in the presence of nanoporous Co-Ni-W-B catalyst at 30 °C is also examined. There is no obvious change in HG with increasing in concentration of AB. This indicates that the hydrolysis of AB by the Co-Ni-W-B catalyst is not dependent on the concentration of AB (Fig. S5, ESI†). It suggests that

hydrolysis is a zero order reaction with respect to the concentration of AB. The observation is consistent with previous report.<sup>22</sup> In order to identify the reaction order with respect to amount of nanoporous Co-Ni-W-B catalyst, the HG rate was measured by using different amounts of nanoporous Co-Ni-W-B catalyst: 0.05, 0.10, 0.15, and 0.20 g. The reaction time required to complete the reaction decreases rapidly with increasing catalyst amount. The HG rate *versus* amount of catalyst is plotted, yielding a fitted straight line (Fig. S6, ESI†). This result clearly indicates that the catalytic hydrolysis reaction of AB is quasi first-order with respect to the amount of catalyst.

The generation of hydrogen with the as-prepared Co-Ni-W-B catalyst in 1 wt% AB solution at different solution temperatures ranging from 30 to 60 °C was monitored (Fig. S7, ESI†). As the temperature increases, the H<sub>2</sub> generation rate of the Co-Ni-W-B catalyst dramatically increases. The initial stage of H<sub>2</sub> generation reaction by the hydrolysis of AB was found to obey zero-order rate law. The reaction rate can be expressed as follows:

$$r = k_0 \exp\left(\frac{-E_a}{RT}\right)$$

where  $k_0$  is the rate constant (mL min<sup>-1</sup> g<sup>-1</sup>),  $E_a$  is the activation energy (kJ mol<sup>-1</sup>),  $R$  is the gas constant (8.3143 kJ (mol K)<sup>-1</sup>), and  $T$  is the reaction temperature (K). Using the zero-order rate constant ( $k$ ) at varied temperatures, an Arrhenius plot of  $\ln r$  (the initial HG rate) *versus* the reciprocal of absolute temperature ( $1/T$ ) is made. From the slope of the straight line, the activation energy of hydrolysis reaction using the nanoporous Co-Ni-W-B catalyst is calculated to be 21.36 kJ mol<sup>-1</sup>. This value of activation energy is lower than the results reported for the hydrolysis of AB catalyzed by the Ru/C (76.0 kJ mol<sup>-1</sup>),<sup>23</sup> Ni<sub>0.99</sub>Pt<sub>0.01</sub> (49.27 kJ mol<sup>-1</sup>),<sup>24</sup> Co-B/SBA-15 (43 ± 2 kJ mol<sup>-1</sup>),<sup>12</sup> Co-Mo-B/Ni foam (44.3 kJ mol<sup>-1</sup>),<sup>15</sup> Cu/RGO (38.2 ± 1.5 kJ mol<sup>-1</sup>),<sup>25</sup> Ru@SiO<sub>2</sub> (38.2 kJ mol<sup>-1</sup>),<sup>26</sup> Cu-Ni (38.2 kJ mol<sup>-1</sup>),<sup>27</sup> Co-W-B/Ni foam (29 kJ mol<sup>-1</sup>),<sup>13</sup> nanoporous nickel spheres (27 ± 1 kJ mol<sup>-1</sup>),<sup>28</sup> and comparable to Co-P (22 kJ mol<sup>-1</sup>),<sup>29</sup> Pt/γ-Al<sub>2</sub>O<sub>3</sub>, Rh/γ-Al<sub>2</sub>O<sub>3</sub>, Ru/γ-Al<sub>2</sub>O<sub>3</sub> (21–23 kJ mol<sup>-1</sup>).<sup>30</sup> As the reaction rate is influenced by the activation energy, nanoporous Co-Ni-W-B catalyst fabricated in this study is shown to be one of the best for the hydrolysis reaction.

To investigate the stability of the nanoporous Co-Ni-W-B catalyst, the catalyst has been tested by the cyclic hydrolysis experiments. The catalyst has been recycled after the completion of the hydrolysis reaction, washed thoroughly with deionized water and loaded into another AB solution. The nanoporous Co-Ni-W-B catalyst shows satisfactory durability in the cyclic usages (Fig. S8, ESI†). The catalyst preserved 87% of its original HG rate at its tenth application, which has better stability than the Co-W-B-P/Ni foam (68% of its original HG rate after tenth usage).<sup>13</sup> It has been shown that the deterioration in catalytic activity of the catalyst used for the hydrolysis of borohydride is attributed to the enriched byproducts on the surface of the catalyst, which decrease the accessibility of active sites. A fast HG rate can help reducing the adsorption of the byproducts on the surface of the catalyst because generated gas blows away the byproducts.<sup>15</sup>

In summary, a novel chemical reduction method based on using ethanol as the reaction medium has been proposed to synthesize nanoporous Co–Ni–W–B catalyst. Compared to the Co–Ni–W–B catalyst prepared in aqueous solution, the nanoporous Co–Ni–W–B catalyst shows high catalytic activity, which is associated with an increased surface area. Preliminary studies have determined the hydrogen generation using the nanoporous Co–Ni–W–B catalyst. Employing the catalyst and 1.0 wt% AB has produced a hydrogen generation rate of 6360 mL min<sup>-1</sup> g<sup>-1</sup> (catalyst). The high performance and low-cost of the nanoporous Co–Ni–W–B catalyst show the promises towards its application in hydrogen generation.

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