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Effects of the Preparation Solvent on the Catalytic Properties of Cobalt–Boron Alloy for the Hydrolysis of Alkaline Sodium Borohydride

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Received: 9 August 2017; Accepted: 10 September 2017; Published: 12 September 2017

Abstract: In this study, the effects of the solvent used to prepare Co–B alloy on its catalytic properties were investigated. The solvent effects on the morphology, composition, and specific surface area of the alloy particles were also examined. The morphology of the alloy particles was found to be dependent on the solvent. The particles were granular in water, methanol, and acetone, although the particle diameters differed, whereas they were nanoflake-like in acetonitrile. Acetonitrile produced the largest surface area of the alloy particles, but the lowest catalytic activity for the hydrolysis of NaBH₄ owing to the ready oxidation of the particles in air. The Co–B in acetone exhibited the highest catalytic activity, represented by a hydrogen generation rate of 5733 mL·min^{−1}·g^{−1} during the hydrolysis of 1.5 wt % NaBH₄ at 298 K. This hydrogen generation rate is more than twice that produced by the Co–B in water.

Keywords: hydrogen generation; NaBH₄; Co–B; hydrolysis; catalytic activity

1. Introduction

Hydrogen has emerged as one of the cleanest energy sources owing to its high efficiency, zero emission, and renewability in recent years [1,2]. However, the safe and efficient production and storage of hydrogen still constitutes a key challenge that restricts the wide application of the gas as an energy source [3–5]. The hydrolysis of sodium borohydride (NaBH₄) has attracted great attention as a promising method for the production of high-purity hydrogen at room temperature, and in a form that satisfies the requirements for use in a fuel cell [6–9]. NaBH₄ has a potential capacity of 10.8 wt % H₂, excellent solubility, and is very stable in water. Furthermore, the byproduct (NaBO₂) of the NaBH₄ hydrolysis process is nontoxic and recyclable. However, the process is kinetically slow in the absence of a suitable catalyst, and this has significantly limited the development of the hydrogen production method [10–12].

Catalysts such as Pt, Ru, Pd, Rh, and other noble metals are very effective to accelerate the hydrolysis reaction of NaBH₄ [13–16]. However, the high cost of these precious metals makes it necessary to explore the alternative non-noble catalysts. Metal borides are such alternative catalysts and can be synthesized in a simple way from their salt solutions. The excellent catalytic activity of metal borides is mainly afforded by their unique properties, which include excellent stability, an amorphous

structure, and many unsaturated sites [17]. Their catalytic activity can be further improved by doping, supporting, and templating [17–21]. Among the available metal borides, Co–B is a leading candidate owing to its outstanding catalytic properties, low cost, and easy preparation [17]. The shortcoming of the conventional Co–B solution prepared using water is the small surface area of the alloy particles and widely distributed particle size. All these detrimental characters result from the exothermic nature of the reduction of Co^{2+} by BH_4^- in the aqueous solution [17].

Various Co-based alloys have been fabricated toward achieving improved catalytic activity by avoiding agglomeration of the alloy particles in solution, through variation of the preparation parameters [22,23]. Although all the employed approaches to producing Co–B alloys have afforded improvement in the catalytic performance, the effect of the solvent has not been well investigated yet. In this work, typical solvents such as acetonitrile, acetone, methanol, and water were adopted to fabricate the Co–B catalyst and the effect on the hydrolysis of NaBH_4 was investigated. These solvents are cheap and widely used in the lab. This work was undertaken with the purpose of providing useful information for enhancing the catalytic properties of Co-based catalysts. The morphology of the Co–B particles in solution was observed to differ with the employed solvent. An acetone solvent was observed to produce the highest activity for the decomposition of NaBH_4 , while the use of acetonitrile afforded the highest surface area. The possible reasons for the solvent effects were also examined.

2. Experimental Section

2.1. Preparation of the Co–B Samples

Analytical grade commercial chemicals were used as received. The Co–B samples were synthesized by the chemical reduction. This involved the dissolution of 39 mmol of CoCl_2 in 100 mL of different solvents, namely, water, methanol, acetone, and acetonitrile, respectively, and vigorously stirring. A 10 mL solution containing 53 mmol NaBH_4 was then added dropwise to the formed suspension. After 6 h of stirring, the black precipitated powder was filtered (pore size 0.2 μm), thoroughly washed, and then dried in vacuum at about 323 K. The detailed instrument information for characterization of the Co–B samples can be found in our previous report [12].

2.2. Hydrogen Generation Measurement

For catalytic activity measurements, an alkaline-stabilized solution, which contained 1.5 wt % NaBH_4 and 5 wt % NaOH , was thermostated in a water bath, and 10 mL of the above solution was then injected into the reaction flask, which contained 0.05 g of the catalyst. The contents of the reaction flask were stirred at a rate of 500 rpm. The temperature of the flask was kept within accuracy ± 0.5 K. The volume of the generated hydrogen was measured by the water replacement method. The weight of the hydrogen was recorded by an electronic balance, which can read the weight automatically. The generated hydrogen volume was normalized by the value under standard temperature and pressure (298 K and 1 atm) [12].

The stability of the catalyst was examined by monitoring the hydrogen generation (HG) rate. The catalyst was collected and thoroughly rinsed using deionized water after the hydrolysis reaction was finished. The same amount of NaBH_4 was then added to the solution to repeat the process, which was repeated four times.

3. Results and Discussion

3.1. Catalyst Characterization

Scanning electron microscopy (SEM) was used to characterize the morphology of the Co–B catalysts. Figure 1 shows the SEM morphologies of the Co–B powder prepared using different solvents. In the cases of the water, methanol, and acetone solvents, the particles can be observed to be aggregated into granular spheres with irregular surfaces, attributable to the strongly exothermic reaction between

Co^{2+} and BH_4^- [24]. Specifically, the diameter of the Co–B particles in the case of the water solvent was about 100 nm (Figure 1a). The particles were smaller when methanol was used as the solvent, their diameter being about 50 nm. In the case of the acetone solvent, the spherical particles were even smaller, their diameter being only about 20 nm. The morphology of the Co–B particles when acetonitrile was used as the solvent was totally different from the other cases, with the particles taking on the form of porous interconnected nanoflakes.

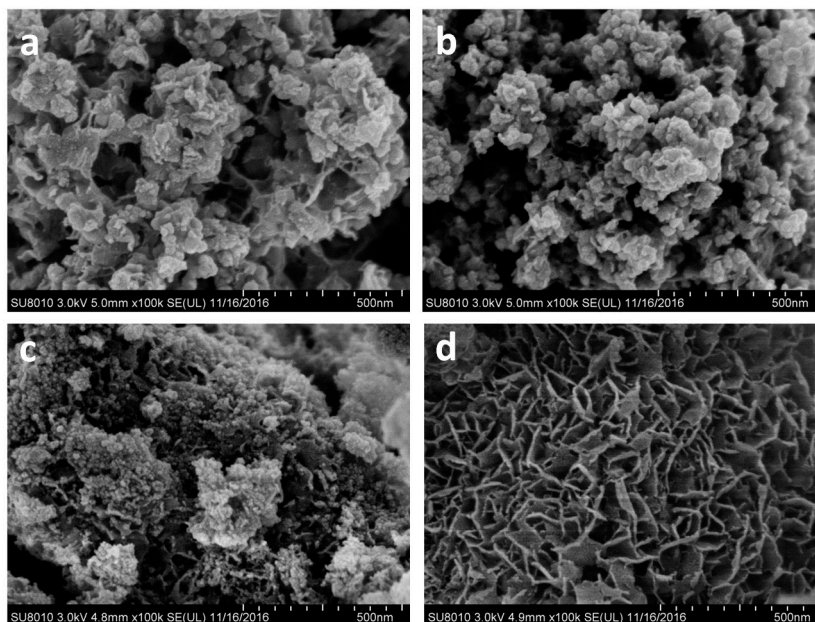


Figure 1. SEM (scanning electron microscopy) micrographs of Co–B particles prepared in (a) water; (b) methanol; (c) acetone; and (d) acetonitrile.

Figure 2 shows the transmission electron microscopy (TEM) images of the Co–B alloy samples prepared using different solvents. It is found that the Co–B particles in water and methanol consist of aggregated nanospheres, while those in acetone are more globally dispersed with a higher degree of uniformity, although there is still some measure of aggregation. Those in acetonitrile have a hierarchical porous structure. Most probably, the nucleations of the Co–B in different solvents were different.

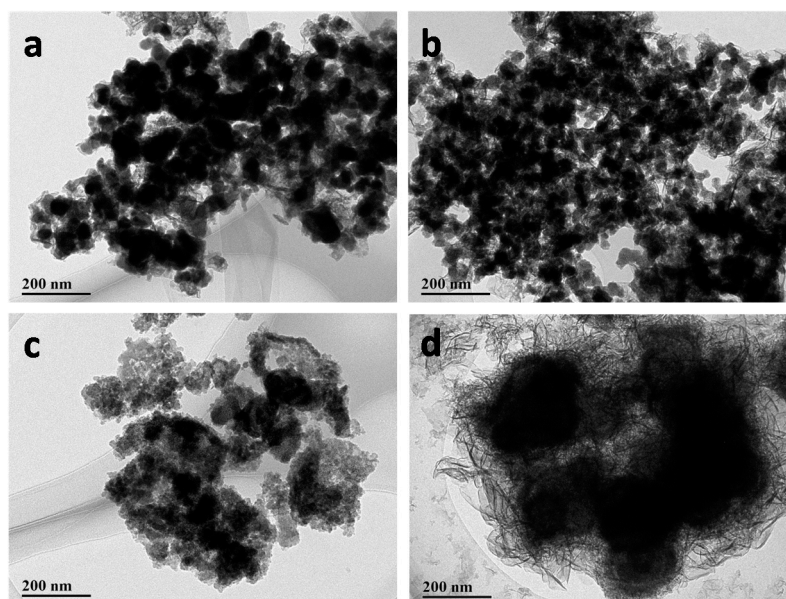


Figure 2. TEM (transmission electron microscopy) images of Co–B particles prepared in (a) water; (b) methanol; (c) acetone; and (d) acetonitrile.

Energy-dispersive X-ray (EDX) analysis further revealed that the Co–B particles in the different solvents consisted of Co, B, and O. The O is possibly from the sample fabrication process through oxidation of the alloy in air. Three areas were analyzed for each sample. The content of each element varied significantly with the solvent used for the preparation. The compositions of the Co–B alloy with respect to the preparation solvent are given in Table 1. It can be observed that the B content of the alloy decreases in the following order: Acetonitrile solvent > acetone solvent > methanol solvent > water solvent. In general, the B atoms are electron deficient in the metal boride and thus readily accept electrons, which is favorable for electron transfer between the catalyst and reactant. This indicates that a greater amount of B is advantageous to the catalytic effect. It has been reported that, with increasing boron concentration in a Co–B alloy, the active Co sites become more highly unsaturated [10]. Hence, the alloy samples prepared in methanol, acetone, and acetonitrile may exhibit higher catalytic activity than that prepared in water. The O content of the Co–B alloy prepared using acetonitrile is fairly high, and this might have inevitably affected its catalytic activity.

Table 1. Composition of Co–B catalysts prepared in different solvents.

Solvent	Co (wt %)	B (wt %)	O (wt %)	Standard Deviation (%)
Water	79.616	4.117	16.267	0.82
Methanol	57.739	4.458	37.803	0.47
Acetone	62.494	5.561	31.945	0.66
Acetonitrile	43.267	13.561	43.217	0.58

Figure 3 shows the wide-range XRD (X-ray diffraction) patterns of the Co–B catalysts. There is no specific peak in any of the patterns, attributable to the amorphous structure of the catalysts, which is in good agreement with the typical structure of Co–B catalysts prepared by chemical reduction [25].

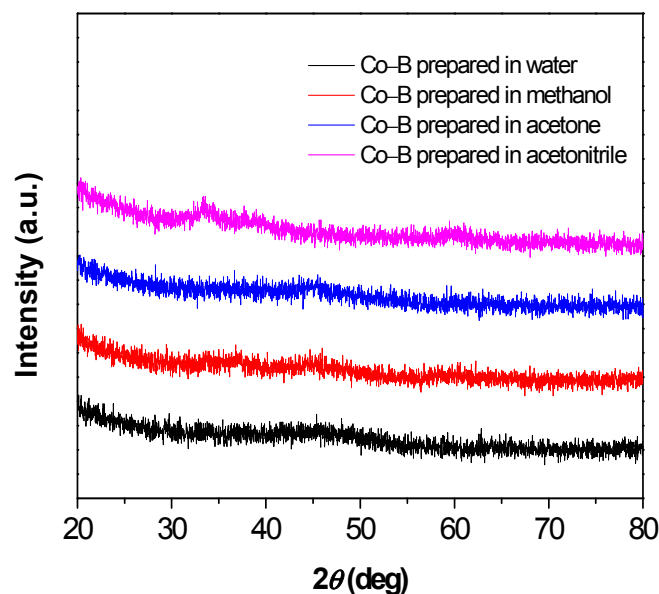


Figure 3. XRD (X-ray diffraction) patterns of Co–B samples prepared in water, methanol, acetone, and acetonitrile.

The surface electronic states were investigated by X-ray photoelectron spectroscopy (XPS). The XPS spectra shown in Figure 4 reveal the binding energies of the Co and B elements in the alloy samples. As can be observed, all the samples demonstrate similar binding energies of the Co 2p^{3/2} (780.9 eV) and B 1s (191.6 eV) species, which are consistent with the reported results [12]. This is suggestive of the character of the amorphous Co–B surface species, and of electron transfer

between the surface B and Co atoms. Two peaks at 796.8 and 780.9 eV correspond to the binding energies of Co $2p^{3/2}$ (indicated with green dash line in Figure 4a), which indicates the elemental and oxidized states of Co existing in the alloy. The Co^{2+} state is related to the peak of the oxidized cobalt and is attributed to the $Co(OH)_2$ species [12]. In the case of the Co–B alloy sample prepared using water, there is a B 1s peak at 188.1 eV (indicated with green dash line in Figure 4b), which corresponds to B^0 (zerovalent B). The binding energy of B in the catalyst shift positively compared with pure B (187.1 eV), which suggests electron transfer from the alloying B to the vacant d-orbital of the metallic Co [26]. For the samples prepared using methanol, acetone and acetonitrile, only the oxidized boron species with a binding energy of 191.6 eV are observed.

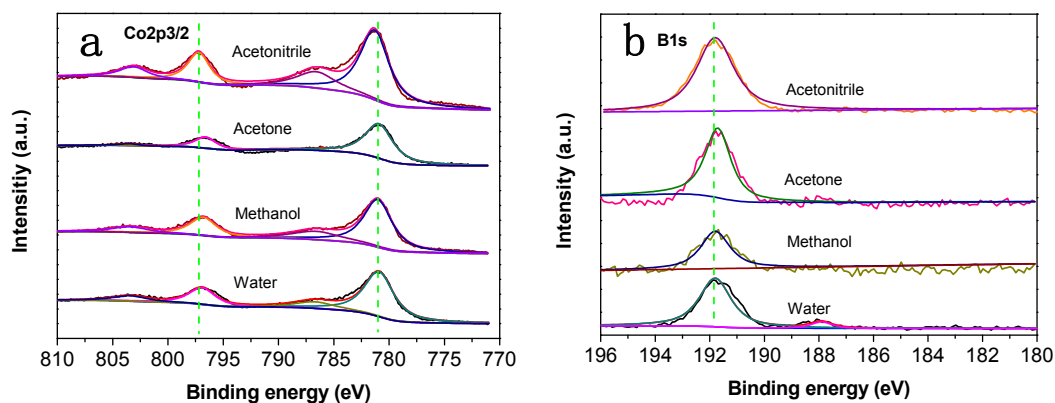


Figure 4. XPS (X-ray photoelectron spectroscopy) spectra of the (a) $Co\ 2p^{3/2}$ and (b) B 1s levels of Co–B powders prepared using water, methanol, acetone, and acetonitrile.

The N_2 adsorption–desorption isotherms were performed at 77 K (Figure 5). The isotherms of the Co–B particles are typical type-IV curves according to the International Union of Pure and Applied Chemistry (IUPAC) classification. Each of the isotherms contains a small hysteresis loop, which indicates many mesopores existed in the samples. The pores provide more active sites for the reactants, as well as an easy exit route for the products. The Brunauer–Emmett–Teller (BET) surface area was calculated to be $364.7\ m^2\cdot g^{-1}$ for the sample of Co–B prepared in acetonitrile, while those of the sample particles prepared in water, methanol, and acetone were 39.7, 51.3, and $117.7\ m^2\cdot g^{-1}$, respectively. The specific surface area (BET), pore volume and pore diameter were summarized in Table 2. The Co–B alloy sample particles prepared in acetonitrile thus had about three times larger surface area than that of the particles prepared in acetone. The pores among the particles were mostly about 5 nm in diameter. Considering the differing surface areas of the different catalyst particles, the parameter might be expected to affect the catalytic activity. Incidentally, it has been reported that B inhibits the aggregation of the alloy particles, and the higher the B content, the higher the surface area of the alloy particles [17]. Furthermore, because the hydrolysis of $NaBH_4$ is a heterogeneous catalytic reaction, the catalytic activity of the catalyst is highly independent on the catalyst particles surface area. It is a fact that the amount of active sites available for the reaction increases with increasing surface area. The samples prepared using organic solvents in the present study thus potentially had higher catalytic activities compared to that prepared using water.

Table 2. Surface area, pore volume, and pore diameter of Co–B catalysts prepared in different solvents.

Solvent	Surface Area ($m^2\cdot g^{-1}$)	Pore Volume ^a ($cm^3\cdot g^{-1}$)	Pore Diameter (nm)
Water	39.7	0.214	10.23
Methanol	51.3	0.249	18.27
Acetone	117.7	0.329	6.83
Acetonitrile	364.7	0.879	5.74

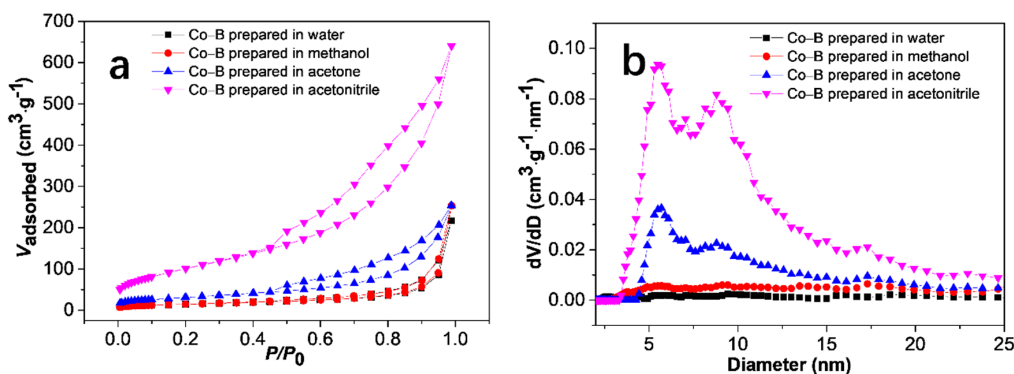


Figure 5. (a) Nitrogen adsorption-desorption isotherms of Co-B powders prepared using water, methanol, acetone, and acetonitrile; and (b) pore size distributions of the Co-B particles.

3.2. Hydrolysis of NaBH₄ Catalyzed by Co-B Alloy

The catalytic activities of the different Co-B catalysts were assessed by the HG during the hydrolysis of NaBH₄ (1.5 wt %) at 298 K. The same amount of catalyst (50 mg) was used in all the different cases. Figure 6 shows the HG results for the Co-B catalysts fabricated using water, methanol, acetone, and acetonitrile, respectively. Hydrogen was instantaneously produced when the NaBH₄ was in contact with the Co-B catalysts. However the HG rates of the different Co-B catalysts decreased in the following order: Acetone solvent > methanol solvent > water solvent > acetonitrile solvent. The highest HG rate of 5733 mL·min⁻¹·g⁻¹ was obtained for the Co-B catalyst prepared in acetone, followed by those prepared in methanol (3080 mL·min⁻¹·g⁻¹) and water (2160 mL·min⁻¹·g⁻¹). Preparation in acetonitrile yielded the lowest HG rate of 1026 mL·min⁻¹·g⁻¹. These results suggest that the catalyst preparation solvent significantly affects the catalytic activity. Although the catalyst prepared in acetonitrile had the highest surface area, its HG rate was the lowest, most probably due to its easier oxidization in air. This was evident from the grey color of the alloy powder after drying in air, compared to the black color of the samples prepared in the other solvents.

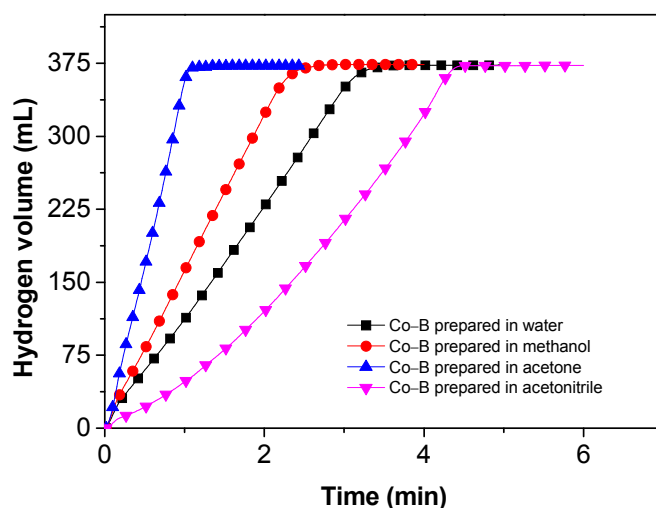


Figure 6. HG (hydrogen generation) from the hydrolysis of NaBH₄ catalyzed by different Co-B alloys as catalysts.

The preparation solvent influences the nucleation of the Co-B alloy catalyst. Because the O-H bond in water is more polarized than those of methanol, acetone, and acetonitrile [27], it induces a stronger adsorption of Co²⁺, resulting in a larger particle size. The phenomenon can also be explained based on the viscosities of water, methanol, and acetone. The viscosity of the solvent is an important

factor for the coordination of its molecules with Co^{2+} . Generally, the precipitation process of the Co–B particles consists of two stages, namely, the nucleation and particle growth stages [28]. Both stages are affected by the solvent viscosity, with an increase in viscosity significantly decreasing the Co^{2+} diffusion rate, resulting in the generation of locally concentrated regions of Co^{2+} . As a result, a lower solvent viscosity decreases agglomeration, thereby increasing the surface area. Hence, the Co–B alloy samples prepared in the higher-viscosity solvents (water) had larger particle sizes and lower surface areas compared to those prepared in methanol and acetone, and were thus more agglomerated [28], as indicated by the SEM and TEM observations. For the Co–B sample prepared in acetonitrile, the reductant NaBH_4 reacted with the solvent, resulting in the generation of other species in the solution. This affected the nucleation of the Co–B in the solution, as evidenced by its very different morphology. The viscosities of the different solvents are presented in Figure 7.

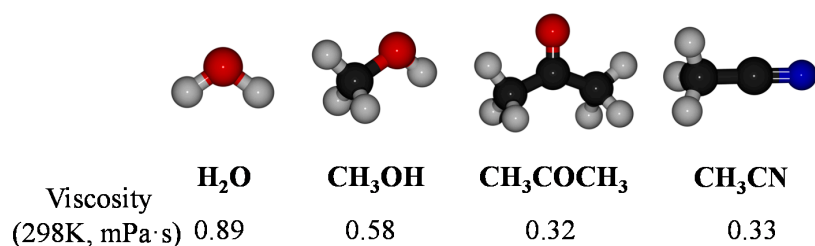


Figure 7. Molecular structures and viscosities of water, methanol, acetone, and acetonitrile at 298 K.

In order to study the kinetics of the hydrolysis of NaBH_4 catalyzed by Co–B particles, the catalyst dosage on the HG was examined. Figure 8 shows plots of the HG of the process versus time for different dosage of the Co–B catalysts. It is clear from the figure that the HG rate increases with increasing amount of the Co–B catalyst used.

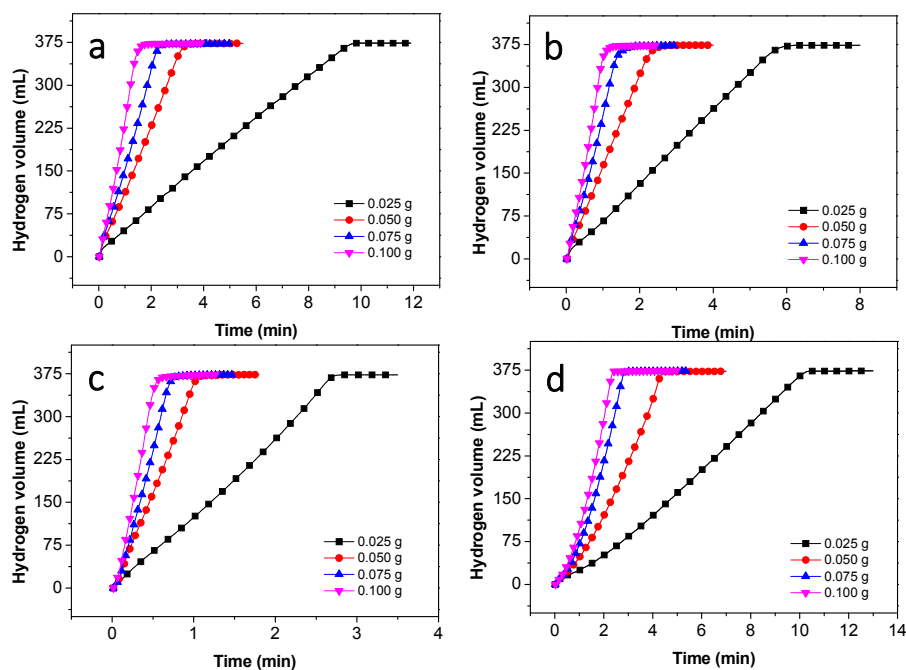


Figure 8. Effect of catalyst dosage on the HG rate for Co–B catalysts prepared in (a) water; (b) methanol; (c) acetone; and (d) acetonitrile. (Batch system; 298 K; 1.5 wt % NaBH_4 .)

Figure 9 shows plots of the HG rate versus the amount of catalyst. It can be observed that the HG rate—increases linearly with the catalyst dosage, indicating that NaBH_4 hydrolysis catalyzed by Co-B nanoparticles is a first-order reaction regarding to the concentration of the Co-B particles.

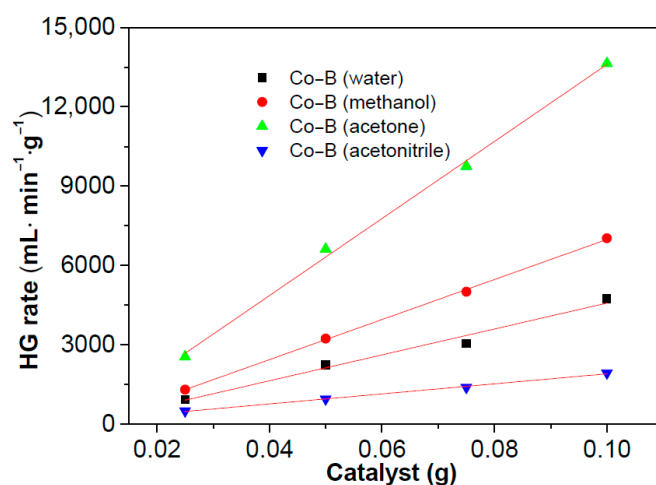


Figure 9. HG rate versus the amount of Co-B catalyst.

The effect of the NaBH_4 concentration on the HG rate was also investigated, which included variation of the initial concentration of the NaBH_4 while maintaining a constant catalyst concentration of 0.05 g. Plots of the HG versus time for the different initial NaBH_4 concentrations are shown in Figure 10. The HG rate can be observed to be almost constant upon NaBH_4 concentration, indicating that the catalytic hydrolysis of NaBH_4 is zeroth order, which is in agreement with a previous report [12]. Theoretically, a higher NaBH_4 concentration increases the hydrogen yield. Nevertheless, the concentration of the byproduct in the hydrolysis solution also increases with increasing NaBH_4 concentration, decreasing the HG rate [29].

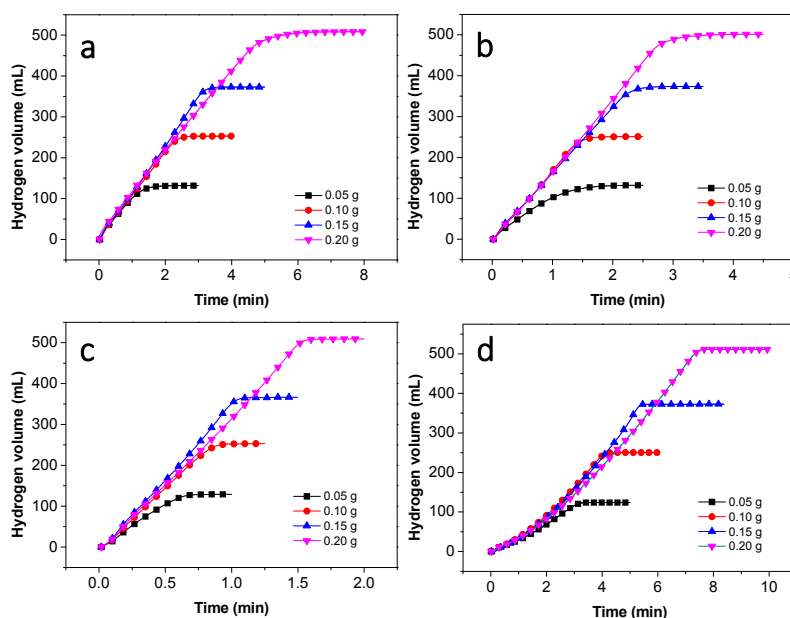


Figure 10. Effect of the NaBH_4 concentration on the HG rate for Co-B catalysts prepared in (a) water; (b) methanol; (c) acetone; and (d) acetonitrile. (Batch system; 298 K; 0.05 g catalyst.)

3.3. Activation Energy of NaBH₄ Hydrolysis Catalyzed by Co–B

To study the effect of temperature on the hydrolysis reaction, a series experiments were performed at different temperatures. Figure 11 shows the plots of HG volume versus the reaction time for different reaction temperatures between 288 K and 318 K. Expectedly, the HG rate increases with increasing reaction temperature.

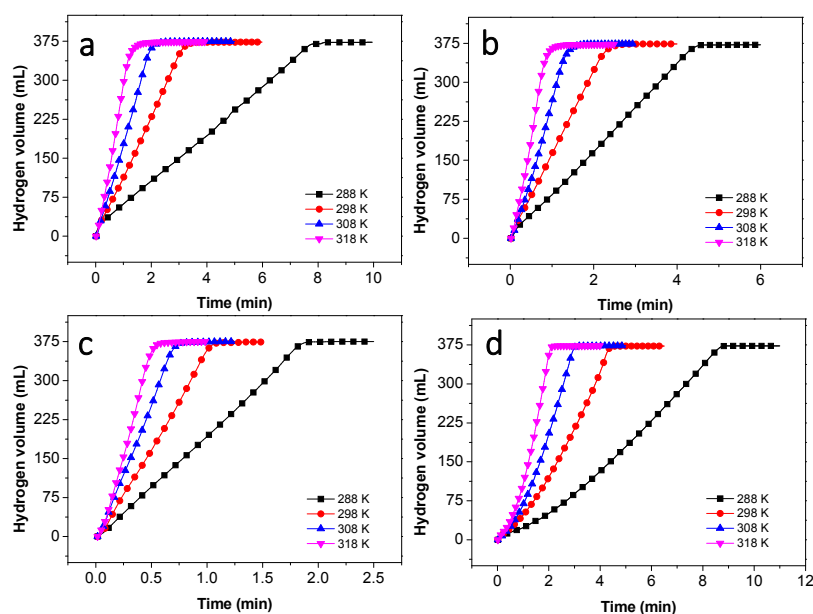


Figure 11. HG kinetics curves for the initial stage of the hydrolysis of 1.5 wt % NaBH₄ at different solution temperatures using Co–B catalysts prepared in (a) water; (b) methanol; (c) acetone; and (d) acetonitrile.

The values of rate constant k were measured from the linear portion of each plot in Figure 11. Arrhenius plots of $\ln k$ of the catalyzed NaBH₄ hydrolysis reaction versus the reciprocal of the absolute temperature ($1/T$) are shown in Figure 12. The activation energy of the hydrolysis reaction was determined to be 37.4, 37.3, 33.3, and 49.3 kJ/mol when using the Co–B alloys prepared in acetone, methanol, water, and acetonitrile respectively. The Co–B alloy prepared in acetone thus produced the lowest activation energy of the NaBH₄ hydrolysis reaction, and the value is comparable with those reported for Co–B based catalysts (see Table 3). This indicates the catalytic superiority of the Co–B alloy prepared in acetone.

Table 3. Activation energy (E_a) values for hydrolysis of NaBH₄ catalyzed by different Co–B catalysts.

Catalyst	E_a (kJ mol ⁻¹)	References
Fishbone-like Co–B	34.2	[10]
Co–B–TiO ₂	36.24	[27]
Co–B–SBA15	43	[30]
Co–B/C	57.8	[31]
Co–B hollow spheres	45.5	[32]
Co–B	43.1	[33]
Co–B prepared in acetone solvent	33.3	Present work

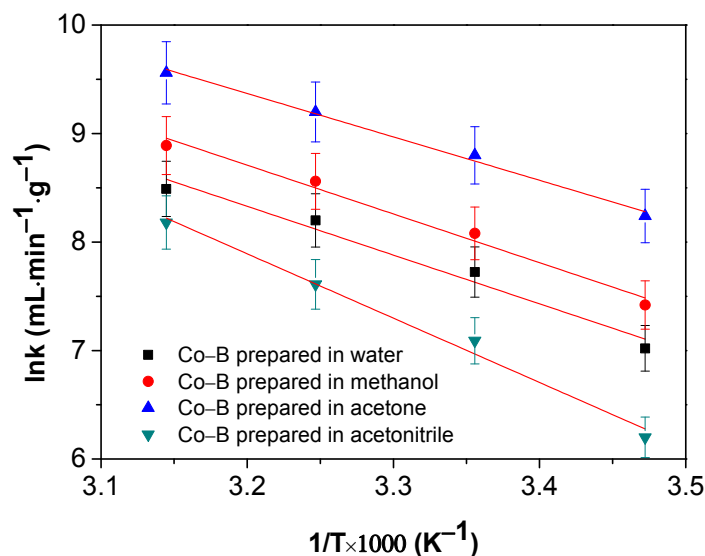


Figure 12. Arrhenius plots of $\ln k$ versus $1/T$.

3.4. Stability of Co–B for Hydrolysis of NaBH_4

The cycle stability of the Co–B alloy prepared in acetone, which produced the highest catalytic activity, was investigated under extended use at 298 K. Ten milliliters of fuel was poured on 0.05 g of the catalyst used to conduct the long-term stability experiment. The plot of the HG versus time is shown in Figure 13, from which it can be observed that the HG rate decreases toward the end of the experiment. This decrease is ascribed to the reaction byproduct covering the active surface area of the catalyst, resulting in poisoning of the catalytic sites, as well as the reduced NaBH_4 concentration [9]. Nevertheless, the catalyst retained ~84.2% of the original value even after ten cycles. It can thus be concluded that Co–B alloy prepared in acetone not only exhibits a high catalytic activity, but also durability. The alloy is therefore a suitable candidate for NaBH_4 hydrolysis for practical applications such as the production of hydrogen fuel.

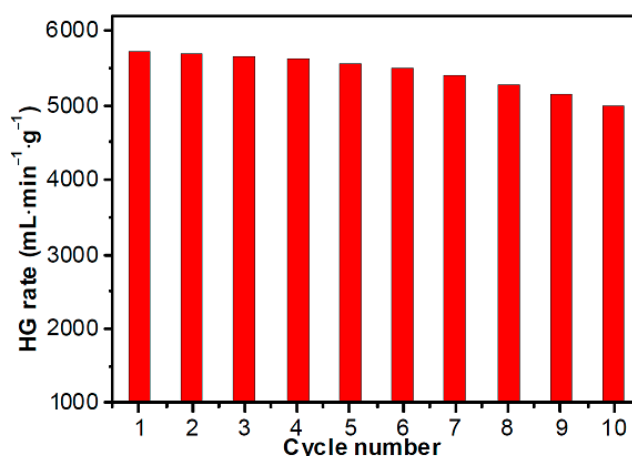


Figure 13. Multicycle performance of Co–B catalyst prepared in acetone for the hydrolysis of 1.5 wt % NaBH_4 at 298 K.

4. Conclusions

Co–B alloy catalysts prepared in different solvents were investigated for hydrogen generation from the hydrolysis of NaBH_4 . The calculated activation energies of the hydrolysis reaction using Co–B alloy catalysts prepared in water, methanol, acetone, and acetonitrile were 37.4, 37.3, 33.3, and 49.3 $\text{kJ}\cdot\text{mol}^{-1}$,

respectively. These results show that acetone is the best solvent among those considered for the preparation of Co–B alloy for this specific purpose, as indicated by the lowest corresponding activation energy, and hence the highest catalytic activity. The Co–B alloy prepared in acetone also exhibited good catalytic stability, which makes it suitable for on-demand hydrogen generation.

Acknowledgments: This work was supported by NSFC (51561006, 11647115, U1501242, 51461010, 51401059, 51361005, 51371060, and 51461011), the GXNSF (2016GXNSFFA380012 and 2014GXNSFAA118318) and Guangxi undergraduate innovation and entrepreneurship training program (201610595187).

Author Contributions: Yongjin Zou and Cuili Xiang initiated the project. Cuili Xiang and Lixian Sun designed and supervised the experimental work, which was performed by Yubo Gao; Pengru Huang, and Hailiang Chu who collected and analyzed the data. Shujun Qiu and Erhu Yan participated in the data analysis. Fen Xu and Yongjin Zou were in charge of writing and checking the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

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