

Short communication

## Sodium borohydride hydrolysis kinetics comparison for nickel, cobalt, and ruthenium boride catalysts

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### Abstract

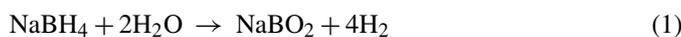
Hydrolysis tests have been performed at a constant temperature of 60 °C over a range of sodium borohydride (2.5–30 wt%) and sodium hydroxide (2.5–30 wt%) concentrations. Catalysts used to initiate the hydrolysis reaction were developed through the metal salt reduction method with sodium borohydride. These catalysts were identified as nickel boride, cobalt boride, and ruthenium with each catalyst having similar morphology. Catalysts were tested in loose, powder form free of binders or substrates. Hydrolysis rate comparisons show that reaction rates decrease linearly with increasing NaBH<sub>4</sub> concentrations due to mass transfer limitations. Increasing NaOH concentration has been shown to drive a non-catalyzed intermediate reaction with the rate of the overall reaction hindered by the catalysts' ability to bind hydrogen to active sites. Maximum hydrogen production rates for the Ni<sub>3</sub>B, Co<sub>3</sub>B, and Ru catalysts were found to be 1.3, 6.0, and 18.6 L min<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>, respectively.

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### 1. Introduction

Sodium borohydride is a reducing agent that has been heavily studied for its usage as a hydrogen carrier. When dissolved in water, it reacts with the solvent to produce four moles of hydrogen. The overall reaction is as follows [1]:



Eq. (1) shows that half of the hydrogen produced in the overall reaction comes from the water solvent. In terms of volumetric density, 30 wt% sodium borohydride solutions store approximately 60 g H<sub>2</sub> per liter. The solution will tend to hydrolyze unless it is kept basic. For this reason, NaOH is added to the solution to keep the pH high. In solution, the mixture is non-toxic, non-flammable and makes the high energy density hydrogen carrier both safe and transportable.

Sodium borohydride can be used directly in a fuel cell and has been shown to achieve high system energy densities [2].

Fuel cells using the hydrogen in the gaseous form, however, exhibit power densities just as any other fuel cell using hydrogen from standard sources, such as high-pressure tanks. Systems have been developed that utilize gaseous hydrogen from sodium borohydride solutions, most notably that of Millenium Cell's Hydrogen On Demand system [3,4].

There are several ways to cause hydrolysis from a base stabilized solution. One obvious method is to lower the pH through the addition of an acid. Early studies focused on acid and metal salt catalysis for sodium borohydride dehydrogenation [1,5–8]. In each of these studies, it was demonstrated that a precipitate was formed during the metal salt catalyzed reaction and that this precipitate could catalyze the hydrolysis reaction at a significant rate. Recently, particular attention has been given to non-noble catalysts produced via metal salt reduction such as cobalt [9], cobalt boride [10–12], nickel boride [13], and nickel-cobalt boride [14]. Similar metal catalysts produced through alternative methods have also been demonstrated as effective catalysts, such as cobalt boride produced through laser deposition techniques [15] and electrodeposition [16].

One particular aspect of the metal catalyzed hydrolysis reaction that is unresolved involves the change in hydrolysis rate with

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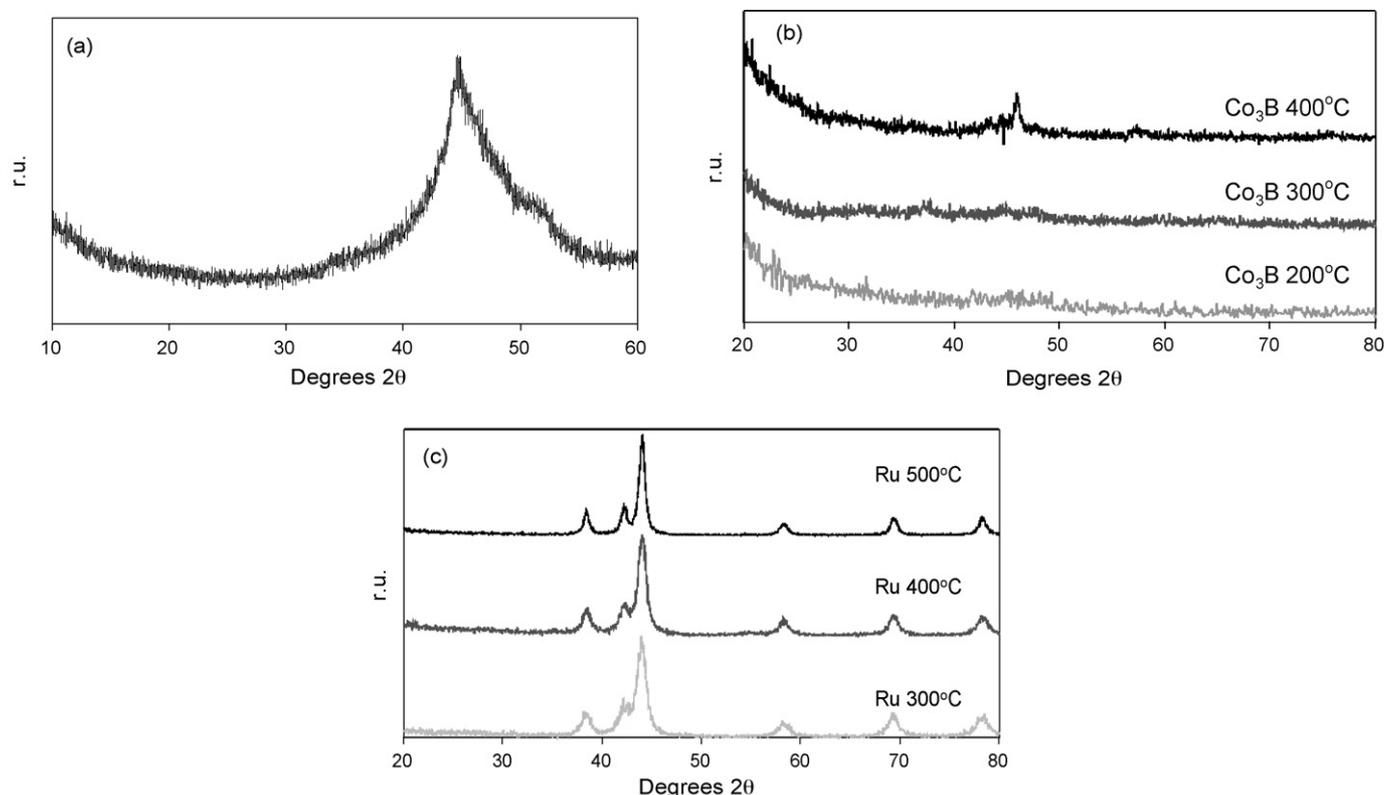


Fig. 1. Catalyst post heat treatment XRD spectra showing crystalline phase growth at higher temperatures, indicative of catalyst composition (a)  $\text{Ni}_3\text{B}$  (b)  $\text{Co}_3\text{B}$ , and (c) elemental Ru.

changing  $\text{NaBH}_4$  and  $\text{NaOH}$  concentration. Amendola et al. [4], Zhang et al. [17], and Jeong et al. [12] have shown that the reaction rate decreases with increasing  $\text{NaBH}_4$  concentration. The work of Kaufman and Sen [6], however, shows that the reaction is zero-order, indicating that a change in concentration should not change the rate of reaction. In terms of the  $\text{NaOH}$  concentration, one would think that increasing the  $\text{NaOH}$  concentration would decrease the hydrolysis rate, especially in the light that the solution is base stabilized to prevent hydrolysis. Work by Jeong et al. using a cobalt boride catalyst shows that the rate of reaction actually increases with increasing  $\text{NaOH}$  concentration [12]. Hua et al. [13] also observed a similar increase in reaction rates when testing nickel boride catalysts, however, observed a decrease in the rate when performing tests with carbon supported ruthenium. Zhang et al. [17] show similar results with their custom catalyst on a nickel substrate. Zhang et al. argue that increasing  $[\text{NaBH}_4]$  increases solution viscosity and, therefore, decreases reaction rate, a deviation from the zero-order kinetics described by Kaufman and Sen [6]. The effect of increasing  $\text{NaOH}$  on the reaction rate is still unresolved, although Zhang theorizes that the rate decrease could stem from slower kinetics between the metaborate ion and the active catalyst sites.

The present study uses catalysts produced from metal salt ( $\text{NiCl}_2$ ,  $\text{CoCl}_2$ ,  $\text{RuCl}_3$ ) reduction in a  $\text{NaBH}_4$  solution to hydrolyze a base stabilized sodium borohydride solution. The resultant catalysts are shown to be similar in morphology. To simplify the analysis, the catalysts were tested in loose, unbound (non-supported) form, alleviating possible mass transfer variations due to the catalyst support or substrate. Each catalyst was

tested over a range of  $\text{NaOH}$  and  $\text{NaBH}_4$  concentrations. Results support zero-order kinetics with respect to  $\text{NaBH}_4$  and show that the decrease is due to mass transfer limitations. The metal catalyzed mechanism of Holbrook and Twist [7] is shown to support the variation in hydrolysis rates with respect to changing  $\text{NaOH}$  concentration. Results indicate that an optimization exists for binary catalysts consisting of noble and non-noble metals.

## 2. Experimental

Catalysts were produced by mixing metal salt solutions with solutions of sodium borohydride at ice bath temperatures, producing a fine black precipitate. Mixing was carried out under nitrogen to prevent oxygen from interacting within the system. The resulting precipitates were rinsed and heat-treated. Heat treatment was performed and the maximum hydrolysis rate was determined as a function of the heat treatment temperature. XRD analysis showed the growth of a crystalline phase for higher heat treatments. This crystalline phase was used to identify the catalyst. The catalysts produced were identified as  $\text{Ni}_3\text{B}$ ,  $\text{Co}_3\text{B}$ , and Ru with the highest catalytic rate occurring for each catalyst at 150, 200, and 400 °C, respectively. SEM images were taken of each sample and showed that the catalyst particles were of similar size and structure. Energy dispersive spectroscopy was also used to ensure that the catalysts were free of impurities. XRD spectra were obtained for the nickel, cobalt, and ruthenium samples and are shown as a function of heat treatment in Fig. 1a–c. Nickel and cobalt were shown to form distinct metal boride peaks, whereas the peaks shown for ruthenium only cor-

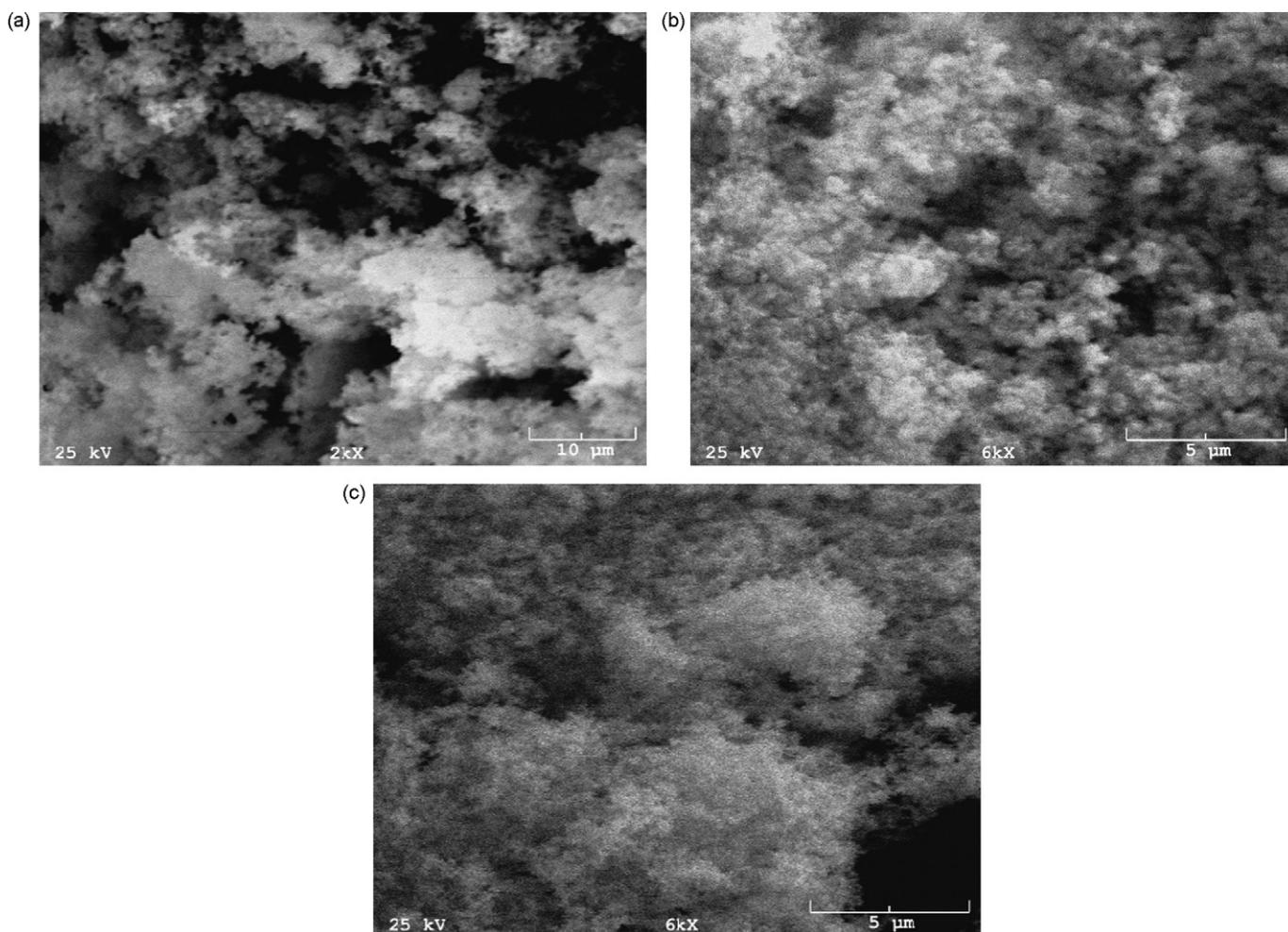


Fig. 2. SEM images of (a)  $\text{Ni}_3\text{B}$ , (b)  $\text{Co}_3\text{B}$ , and (c) Ru catalysts.

respond to elemental ruthenium. Nickel boride catalysts have been developed previously by Jasinski [18] and Hua et al. [13], who have shown the heat treatment temperature to be around  $150^\circ\text{C}$ . SEM images of the optimally heat-treated samples are shown in Fig. 2a–c.

Hydrolysis experiments were performed to test the hydrogen generation rate of the prepared catalysts as a function of  $\text{NaBH}_4$  and  $\text{NaOH}$  concentration. Appropriate wt% solutions were made by adding specific amounts of  $\text{NaOH}$  and  $\text{NaBH}_4$  to 15 g of water. The prepared solutions were placed into a 75 mL flask with temperature maintained via a water bath held at  $60^\circ\text{C}$ . Once the solution reached thermal equilibrium with the surrounding bath, the catalyst was added to the solution in loose, powder form. Once in the solution, the catalyst powder dispersed throughout the bottom of the solution and evolved hydrogen caused ample circulation within the flask. The reaction chamber was then sealed, except for a small tube that transferred the evolved hydrogen to a water displacement system at room temperature. The volume of water displaced was measured over time using a graduated cylinder to determine the hydrolysis rate.

Hydrolysis tests for each catalyst were performed from 2.5 to 30 wt%  $\text{NaBH}_4$  with the  $\text{NaOH}$  concentration being constant for each test, 5 wt%. The same set of tests was then performed

with the  $\text{NaOH}$  concentration varying from 2.5 to 30 wt% while the  $\text{NaBH}_4$  concentration was held constant at 20 wt%. Table 1 gives the maximum rate,  $\text{NaBH}_4$  concentration, and  $\text{NaOH}$  concentration determined for each type of catalyst. This maximum rate was then used to normalize the rates found for each catalyst at the concentration tested. This allows for direct comparison of the  $\text{NaBH}_4$  concentration changes and its effect on the reaction rate for the  $\text{Ni}_3\text{B}$ ,  $\text{Co}_3\text{B}$ , and Ru catalysts. Fig. 3 shows the nor-

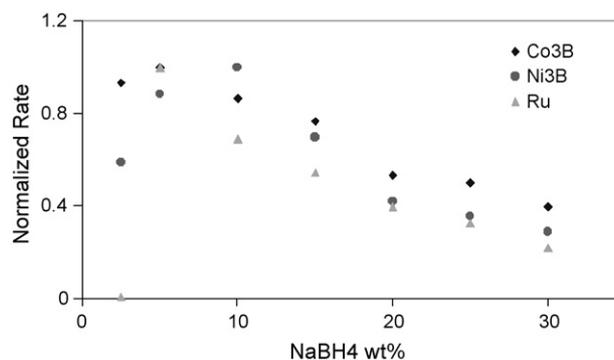


Fig. 3. Comparison of hydrolysis rates normalized to the maximum observed rate for each type of catalyst from 2.5 to 30 wt%  $\text{NaBH}_4$  with  $\text{NaOH}$  constant at 5 wt%.

Table 1  
Maximum hydrolysis rates for solutions at 60 °C with given NaBH<sub>4</sub> and NaOH solution concentrations for each set of concentration tests

	X wt% NaBH <sub>4</sub>			X wt% NaOH		
	<i>r</i> <sub>max</sub> (mL min <sup>-1</sup> g <sup>-1</sup> )	NaBH <sub>4</sub> (wt%)	NaOH (wt%)	<i>r</i> <sub>max</sub> (mL min <sup>-1</sup> g <sup>-1</sup> )	NaBH <sub>4</sub> (wt%)	NaOH (wt%)
Ni <sub>3</sub> B	1289	10	5	1280	20	30
Co <sub>3</sub> B	6000	5	5	4880	20	30
Ru	18596	5	5	8560	20	5

malized rate of hydrogen generation at atmospheric condition and 60 °C for 0.05 g of Ni<sub>3</sub>B, 0.03 g of Co<sub>3</sub>B, and 0.01 g Ru catalyst tested at a constant [NaOH] of 5 wt%.

### 3. Discussion

The decrease in the rate for each catalyst is linear with increasing NaBH<sub>4</sub> concentration. The slopes of the rate data shown in Fig. 3 are 0.029, 0.024, and 0.029 1/[NaBH<sub>4</sub>] for Ni<sub>3</sub>B, Co<sub>3</sub>B, and Ru, indicating that the change in reaction rate is independent of the catalyst for [NaBH<sub>4</sub>] greater than 5 wt%. Because the catalysts are structurally very similar, this is conclusive evidence that the reaction is mass transfer limited.

The trends shown in Fig. 4 indicate that the same does not hold true in the case of increasing [NaOH]. Ni<sub>3</sub>B and Co<sub>3</sub>B exhibit an increase in reaction rate with increasing NaOH concentration, up to the point of solution saturation (>30 wt%). The normalized rate for the Ni<sub>3</sub>B catalyst increased roughly by a factor of three, yet the Co<sub>3</sub>B rate increased by only a factor of one-half. Fig. 3 shows that the tests in Fig. 4 are being conducted in a mass transfer limited concentration range, i.e. [NaBH<sub>4</sub>] is greater than 5 wt%. The increased reaction rate exhibited by Ni<sub>3</sub>B and Co<sub>3</sub>B can be explained if a non-catalyzed intermediate reaction is [NaOH] dependant. Such an intermediate reaction is given in the mechanism proposed by Holbrook and Twist [7], who developed the following reaction scheme based on tests using D<sub>2</sub>O and H<sub>2</sub>O:

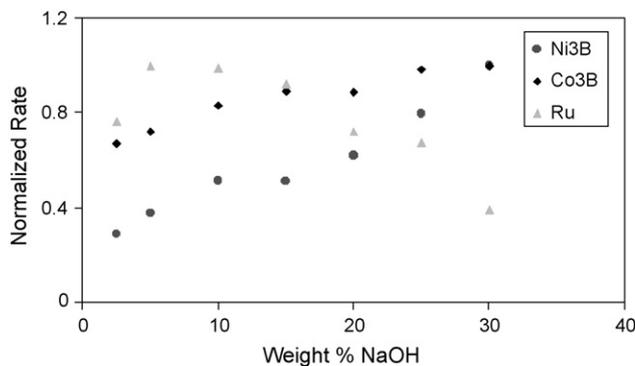
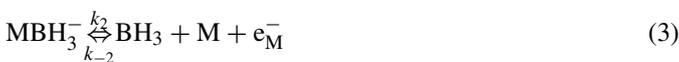


Fig. 4. Comparison of hydrolysis rates normalized to the maximum observed rate for each type of catalyst from 2.5 to 30 wt% NaOH with NaBH<sub>4</sub> constant at 20 wt%.



Holbrook and Twist showed that the reaction begins with the attachment of the borohydride ion to a catalytic site, forming two metal complexes. The MBH<sub>3</sub><sup>-</sup> complex is then in equilibrium with BH<sub>3</sub> in what Holbrook and Twist refer to as the anodic step. The rate of the reaction is determined by the cathodic step also known as the Volmer reaction (5), where an electron is combined with a water molecule and an available site to form the MH complex and the hydroxyl ion. This is under the assumption that the reactivity of the BH<sub>3</sub>(OH)<sup>-</sup> ion is similar to that of BH<sub>4</sub><sup>-</sup>, establishing an equilibrium condition. The complexes formed, MBH<sub>2</sub>(OH)<sup>-</sup> and MH, further reduce in the same process shown in steps similar to that of (2)–(4) [7,19]. The rate constant, *k*<sub>3</sub>, is an uncatalyzed rate. An increase in [NaOH] would then drive (3) forward. This can be shown using the equilibrium condition of reactions (1) and (2) and assuming that the reverse reaction, *k*<sub>-3</sub> is small or non-existent.

$$K_1 = \frac{[MBH_3^-][MH]}{[BH_4^-][M]^2} \quad (7)$$

and

$$K_2 = \frac{[BH_3][M]}{[MBH_3^-]} \quad (8)$$

Again, assuming small *k*<sub>-3</sub>, the catalyst-independent expression for the rate of reaction (4) can be written as:

$$-\frac{d[BH_3]}{dt} = k_3[BH_3][OH^-] \quad (9)$$

Solving (8) for [BH<sub>3</sub>] and substituting into (9) gives:

$$-\frac{d[BH_3]}{dt} = \frac{k_3 K_2 [MBH_3^-][OH^-]}{[M]} \quad (10)$$

Solving for [MBH<sub>3</sub><sup>-</sup>] in (7) and substituting into (10) gives:

$$-\frac{d[BH_3]}{dt} = \frac{k_3 K_1 K_2 [BH_4^-][OH^-][M]}{[MH]} \quad (11)$$

Recognizing that

$$-\frac{d[BH_3]}{dt} = -\frac{d[BH_4^-]}{dt} \quad (12)$$

it is seen that the reaction rate increases linearly with increasing [OH<sup>-</sup>] and decreases linearly with the number of sites

that are occupied with hydrogen. Increasing the rate of (4) tends to increase [MH] through the repeating reaction where  $\text{BH}_3(\text{OH}^-) \rightarrow \text{BH}_2(\text{OH}^-)_2 \rightarrow \text{BH}(\text{OH}^-)_3 \rightarrow \text{B}(\text{OH}^-)_4$  via the same mechanism as (2) through (4). In cases where the catalyst does not strongly bind the hydrogen, the [MH] complex formed during the repeated reaction is rapidly converted to the overall reaction product, hydrogen. If we consider that noble, platinum group catalysts such as ruthenium can exhibit a strong affinity for hydrogen, then (6) can approach an equilibrium condition such that:

$$K_5 = \frac{[\text{M}]^2}{[\text{MH}]^2} \quad (13)$$

Combining (11), (12), and (13) one obtains the catalyst and  $[\text{OH}^-]$  dependent rate:

$$-\frac{d[\text{BH}_4^-]}{dt} = k_3 K_1 K_2 K_5^{1/2} [\text{OH}^-] [\text{BH}_4^-] \quad (14)$$

During the constant temperature tests,  $k_3$  remains unchanged. When a hydrogen adsorbing catalyst is used, such as ruthenium, the increase in NaOH pushes (3) forward increasing [MH] and thereby increases  $k_1$  and reduces the overall reaction rate. The reversing rate trend with increasing NaOH shown in Fig. 4 is supported by (14) and additionally reveals that for catalysts such as Ru, the hydrogen release rate, (6), can limit the overall reaction rate. Fig. 4 also shows that this effect is less significant for Co, and least significant for Ni, as seen from transition of slopes in Fig. 4 from positive to negative.

#### 4. Conclusion

Overall, Ru catalyzed reactions yielded the highest reaction rates, followed by  $\text{Co}_3\text{B}$  and  $\text{Ni}_3\text{B}$ . When varying  $[\text{NaBH}_4]$ , the highest rates occurred between 5 and 10 wt% for each catalyst. Each catalyst showed a decreased reaction rate above 10 wt%  $\text{NaBH}_4$ . The  $\text{Ni}_3\text{B}$ ,  $\text{Co}_3\text{B}$ , and Ru catalysts each show roughly a three-fold decrease in reaction rate at 30 wt% as compared to the maximum rate for each catalyst. Increasing  $[\text{NaOH}]$  concentration increased the reaction rate for the non-noble metal boride catalysts; however, the rate decreased for the noble, ruthenium catalyst. By testing the catalysts free of substrate or binder, mass transfer effects were made uniform amongst the three catalysts examined. Changes in the rate due to varying  $[\text{NaOH}]$  concentration can be explained through previously proposed mechanisms, where initial hydroxyl concentration establishes the overall reaction equilibrium condition. This increases the rate at which [MH] is formed. Catalysts that bind hydrogen strongly can thereby exhibit decreased hydrogen generation rates due to increasing  $[\text{OH}^-]$ , while catalysts that allow rapid formation of  $\text{H}_2$  from the MH complexes can exhibit higher reaction rates at higher  $[\text{OH}^-]$ .

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