



# Hydrogen generation from hydrolysis of ammonia-borane using Pd–PVB–TiO<sub>2</sub> and Co–Ni–P/Pd–TiO<sub>2</sub> under stirred conditions

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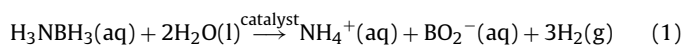
## ABSTRACT

The employment of Pd–PVB–TiO<sub>2</sub> and Co–Ni–P/Pd–TiO<sub>2</sub> in hydrogen generation from the hydrolysis of ammonia-borane (H<sub>3</sub>NBH<sub>3</sub>, AB) under stirred conditions are reported. Both catalysts are found to be highly active, isolable, and reactivatable in the hydrolysis of ammonia-borane even at low concentrations and temperature. The Arrhenius activation energies were found to be 54.9 and 54.7 kJ mol<sup>-1</sup> for the hydrolysis of ammonia-borane catalyzed by Pd–PVB–TiO<sub>2</sub> and Co–Ni–P/Pd–TiO<sub>2</sub>, respectively. Maximum hydrogen generation rates in the hydrolysis of AB catalyzed by the Pd–PVB–TiO<sub>2</sub> catalyst (1.5 mM) are 1910 and 14,800 mL H<sub>2</sub> min<sup>-1</sup> (g Pd)<sup>-1</sup> at 25 and 55 ± 0.5 °C, respectively. The maximum hydrogen generation rates are 170 and 1390 mL H<sub>2</sub> min<sup>-1</sup> (g catalyst)<sup>-1</sup> for the hydrolysis of AB catalyzed by Co–Ni–P/Pd–TiO<sub>2</sub> (25 mg) at 25 °C and 55 ± 0.5 °C, respectively. In comparison to unstirred conditions, these results demonstrate that a significant external mass transfer resistance caused by the desorbed metaborate by-products exist in the under unstirred conditions.

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## 1. Introduction

Fuel cells are attractive and alternative options for producing clean energy for transportation and portable electronic applications [1–3]. Recently, proton exchange membrane fuel cells (PEMFCs) using hydrogen as fuel have been extensively studied as an energy source due to their high efficiency, high power density, and zero emission of environmental pollutants [4–7]. Development of a safe and convenient hydrogen storage and production system is essential for the successive use of PEMFCs. Among the new hydrogen storage materials [8,9], AB appears to be the most promising solid hydrogen carrier [10–13] owing to its combined advantages of; (i) high hydrogen content (19.6 wt%) [14,15], (ii) high solubility in water [10], (iii) high stability in aqueous solution with respect to self-hydrolysis [3], and (iv) its ability to generate hydrogen upon hydrolysis (Eq. (1)) at room temperature in the presence of a suitable catalysts [1,3–5].



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In order to employ H<sub>2</sub> as a direct fuel supply for proton exchange membrane fuel cells, a suitable catalyst is needed to accelerate the hydrolysis of AB [16]. Therefore, the development of efficient, low-cost, and stable catalysts to further improve the hydrolysis of AB under moderate conditions is important for practical applications [17,8]. A number of catalysts have been identified to be effective for accelerating the hydrolysis reaction of AB, including various transition metal salts RuCl<sub>3</sub>, PdCl<sub>2</sub>, and CoCl<sub>2</sub> [18], noble metal nanoclusters and non noble metals supported on γ-Al<sub>2</sub>O<sub>3</sub>, carbon, and SiO<sub>2</sub> [2,7], solid acid catalysts [3], K<sub>2</sub>PtCl<sub>6</sub> [11], Ni<sub>1-x</sub>Pt<sub>x</sub> hollow spheres [19], Ru/C [20], colloidal Rh(0), Ir(0), and Co(0) catalysts [21], Cu@Cu<sub>2</sub>O core shell catalysts [22], hollow Ni–SiO<sub>2</sub> nanosphere [23], Pt- and Ni-based alloys [24], Fe(0) nanoparticles [25], PVP-stabilized nickel(0) [26] and cobalt(0) nanoclusters [27], polymer-stabilized ruthenium(0) and palladium(0) nanoclusters [28], magnetically recyclable Fe–Ni alloy [17], cobalt(0) nanoparticles [29], water/air-stable Ni nanoparticles [30], Pt<sub>x</sub>Ni<sub>1-x</sub> nanoparticles [31], zeolite confined copper(0) [32], palladium(0) [33], cobalt(0) [34], and nickel(0) nanoclusters [35], cobalt–molybdenum–boron/nickel foam [36], hollow Co–B nanospindles [37], nanoparticle-assembled Co–B thin film [38], bimetallic Au–Ni nanoparticles embedded in SiO<sub>2</sub> nanospheres [39], Cu/Co<sub>3</sub>O<sub>4</sub> nanoparticles [40], electroless Co–Ni–P/Pd–TiO<sub>2</sub> [41], Pd–PVB–TiO<sub>2</sub> [42], SiO<sub>2</sub> supported monodisperse nickel nanoparticles [43], and Co–SiO<sub>2</sub> nanosphere [44].

In the previous studies [41,42], we reported the preparation, characterization, and employment of the electrolessly deposited

Co–Ni–P/Pd–TiO<sub>2</sub> and polymer immobilized Pd–PVB–TiO<sub>2</sub> as active and reactivatable catalysts for hydrogen generation from the hydrolysis of AB under unstirred conditions. The study for the unstirred condition is most useful for devices (such as laptops and cell phones) that requires non-bulky hydrogen generators. The inclusion of a stirring mechanism for the catalyst in hydrogen generators will increase the complexity and bulkiness of the design. Herein, we report the catalytic activity of Co–Ni–P/Pd–TiO<sub>2</sub> and Pd–PVB–TiO<sub>2</sub> catalysts in the hydrolysis of AB under stirred conditions. The kinetics of the hydrolysis reaction was studied by measuring the volume of generated hydrogen gas varying catalyst concentration, substrate concentration, and temperature under stirring. The results are compared with those obtained under unstirred conditions. Stirring in the present work is critical not only for the improvement in the mass transport of the reactants but for the role it plays with respect to the catalyst deactivation that results from a possible coverage of the catalyst active sites (similar to coking) with ammonium borate – a byproduct of the hydrolysis reaction. It is to be noted that stirring does not change the mechanism of the reaction. The high catalytic activity and reusability of the Co–Ni–P/Pd–TiO<sub>2</sub> and Pd–PVB–TiO<sub>2</sub> under stirring make them promising candidates to be used as catalysts in developing highly efficient portable hydrogen generation systems using AB as solid hydrogen storage material.

## 2. Experimental

### 2.1. Chemicals

Palladium(II) acetate (98%), ammonia-borane complex (97%), titanium dioxide (Degussa P-25), ammonium hydroxide, cobalt sulfate heptahydrate, nickel sulfate hexahydrate, sodium hypophosphite monohydrate, EDTA, gluconic acid, boric acid, sodium potassium tartrate, and methanol were purchased from Aldrich. Poly vinyl butyral (PVB, butvar, B98) was supplied by Solutia (St. Louis, MO, USA). All chemicals were used as received. Deionized water was distilled by water purification system. All glassware and Teflon coated magnetic stir bars were cleaned with acetone, followed by copious rinsing with distilled water before drying in an oven at 100 °C. The detailed information on the preparation and characterization of the Pd–PVB–TiO<sub>2</sub> [42] and Co–Ni–P/TiO<sub>2</sub> [41] catalysts can be found elsewhere.

### 2.2. Method to test the catalytic activity of Pd–PVB–TiO<sub>2</sub> or Co–Ni–P/Pd–TiO<sub>2</sub> catalyst in the hydrolysis of ammonia-borane

The catalytic activity of the Pd–PVB–TiO<sub>2</sub> or Co–Ni–P/Pd–TiO<sub>2</sub> catalyst in the hydrolysis of AB was determined by measuring the rate of hydrogen generation. In all the experiments, the reaction flask (30 mL) was placed in a thermostat that was equipped with a water circulating system, wherein the temperature was kept constant at 25 ± 0.5 °C. Then, a graduated buret (50 mL) filled with water was connected to reaction flask to measure the volume of the hydrogen gas to be evolved from the reaction. The reliability of water-displacement method for the estimation of evolved gas is based on literature including the recent work of Basu et al. [20] who estimated ±0.7% experimental error with the evaluation approach for the moles of hydrogen collected. Next, 31.8 mg (1.0 mmol) AB was dissolved in 20 mL water (50 mM AB, corresponds to 3 mmol H<sub>2</sub>). This solution was transferred with a glass pipette into the reaction flask thermostated at 25 ± 0.5 °C. Then, certain amount of Pd–PVB–TiO<sub>2</sub> or Co–Ni–P/Pd–TiO<sub>2</sub> catalyst was added into the reaction flask. The reaction was started by closing the flask and turning the magnetic stirrer on at 900 rpm. The volume of hydrogen gas evolved was measured by recording the displacement

of water level from the graduated buret as the reaction progressed. A detailed sketch of the experimental set-up used for performing the catalytic hydrolysis of ammonia borane and measuring the volume of hydrogen gas evolved is given in [41,42].

### 2.3. Control experiments

#### 2.3.1. Self-hydrolysis of ammonia-borane

In order to determine the rate of the self-hydrolysis of AB in the absence of catalyst, 1 mmol (31.8 mg) H<sub>3</sub>NBH<sub>3</sub> was dissolved in 20 mL water and the solution was transferred into the reaction flask thermostated at 25 ± 0.5 °C. The reaction flask was closed and the reaction was started. The volume of generated hydrogen gas was measured exactly in the same way as described in the Section 2.2. It was found that in the self-hydrolysis of AB after 1 day, there is no hydrogen gas generation. This result indicates that AB is highly stable toward hydrolysis in aqueous solution as reported in the literature [36].

#### 2.3.2. TiO<sub>2</sub>-catalyzed hydrolysis of ammonia-borane

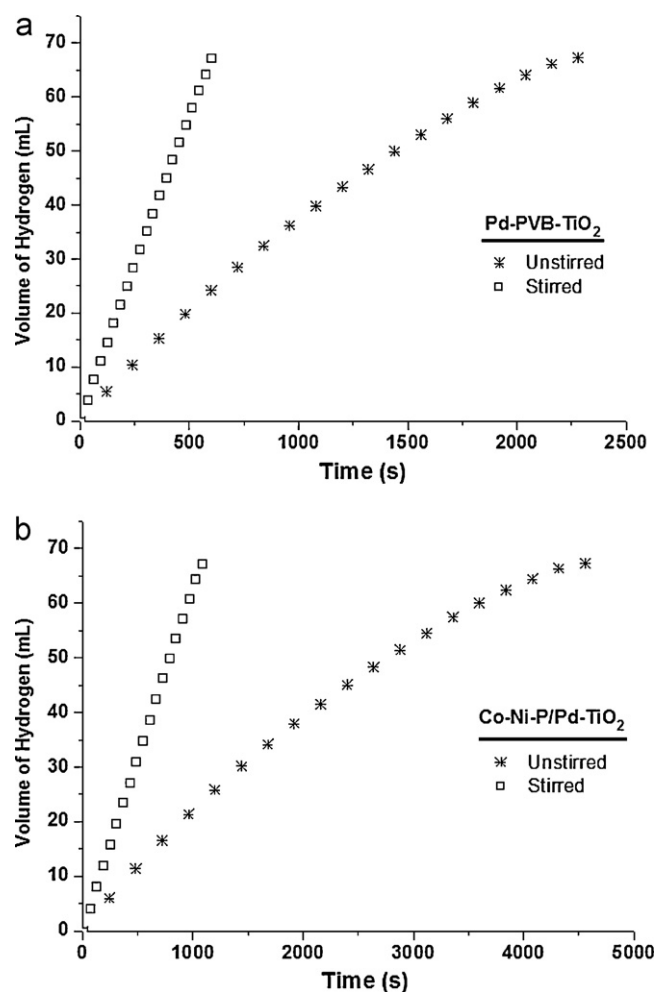
In order to check the catalytic activity of titanium dioxide in the hydrolysis of AB and to make correction, if necessary, in the expression of the catalytic activity of the catalysts, the catalytic activity of TiO<sub>2</sub> (100 mg) in the hydrolysis of H<sub>3</sub>NBH<sub>3</sub> (31.8 mg in 20 mL) was performed at 25 ± 0.5 °C by following the same way described in the Section 2.2. Since no hydrogen gas evolution was observed in the TiO<sub>2</sub>-catalyzed hydrolysis of AB after 6 h, it is not necessary to make any correction on the obtained kinetic data.

### 2.4. Kinetic study of the hydrolysis of the ammonia-borane catalyzed by Pd–PVB–TiO<sub>2</sub> or Co–Ni–P/Pd–TiO<sub>2</sub> catalyst

In order to establish the rate law for the hydrolysis of AB using Pd–PVB–TiO<sub>2</sub> or Co–Ni–P/Pd–TiO<sub>2</sub> as catalyst, two different sets of experiments were performed in the same way described in Section 2.2. In the first set of experiments, the hydrolysis reaction was carried out starting with different initial catalyst concentration/amount (0.5, 1.0, 1.5, 2.0, and 2.5 mM for Pd–PVB–TiO<sub>2</sub> or 25, 50, 75, and 100 mg for Co–Ni–P/Pd–TiO<sub>2</sub>) and keeping the initial AB concentration constant (50 mM). The second set of experiments was carried out by keeping the initial catalyst concentration/amount constant (1.5 mM for Pd–PVB–TiO<sub>2</sub> or 25 mg for Co–Ni–P/Pd–TiO<sub>2</sub>) and varying the AB concentration (50, 100, and 150 mM). Finally, the hydrolysis of AB was carried out by keeping the AB (50 mM) and catalyst concentration/amount (1.5 mM for Pd–PVB–TiO<sub>2</sub> or 25 mg for Co–Ni–P/Pd–TiO<sub>2</sub>) constant at temperatures of 25, 35, 45, and 55 ± 0.5 °C in order to obtain the activation energy ( $E_a$ ) for this hydrolysis reaction. The catalyst/AB mixture was stirred at 900 rpm during the course of each experiment.

### 2.5. Isolability and reusability of the Pd–PVB–TiO<sub>2</sub> and Co–Ni–P/Pd–TiO<sub>2</sub> catalysts in the hydrolysis of ammonia-borane

After the first run of the hydrolysis of 50 mM H<sub>3</sub>NBH<sub>3</sub> (31.8 mg in 20 mL), catalyzed by Pd–PVB–TiO<sub>2</sub> and Co–Ni–P/Pd–TiO<sub>2</sub> catalyst (1.5 mM for Pd–PVB–TiO<sub>2</sub> or 25 mg for Co–Ni–P/Pd–TiO<sub>2</sub>) at 25 ± 0.5 °C, the catalysts were isolated, washed with deionized water and methanol, and dried in the oven at 60 °C. The isolated and dried samples of the Pd–PVB–TiO<sub>2</sub> and Co–Ni–P/Pd–TiO<sub>2</sub> catalyst were used again in the hydrolysis of 50 mM AB and the same procedure was repeated five times. The results were expressed in terms of retained percent catalytic activity of the Pd–PVB–TiO<sub>2</sub> and Co–Ni–P/Pd–TiO<sub>2</sub> catalyst and conversion of AB in the hydrolysis of AB solution.

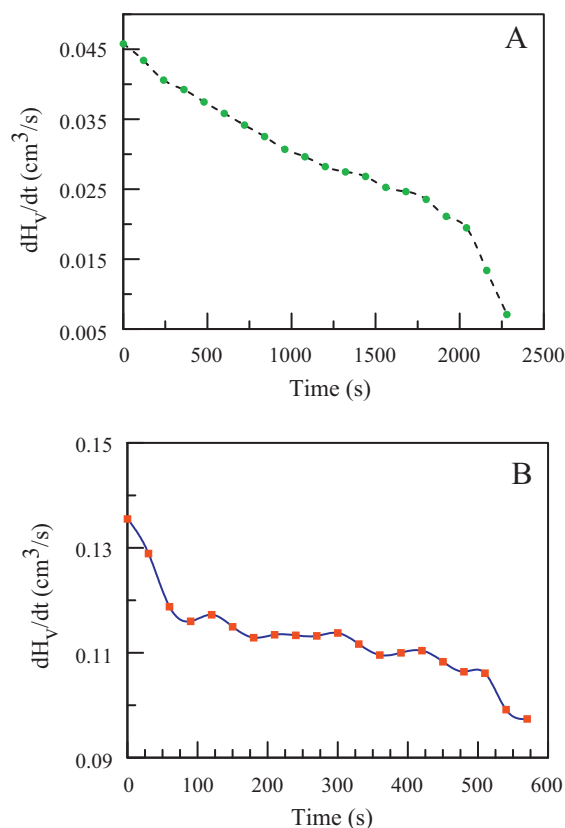


**Fig. 1.** The volume of hydrogen versus time plots for the hydrolysis of ammonia-borane in the presence of (a) Pd-PVB-TiO<sub>2</sub> (2.0 mM Pd) and (b) Co-Ni-P/Pd-TiO<sub>2</sub> (25 mg) catalysts under both unstirred and stirred conditions.

### 3. Results and discussion

#### 3.1. Kinetic study of the hydrolysis of ammonia-borane catalyzed by Pd-PVB-TiO<sub>2</sub> or Co-Ni-P/Pd-TiO<sub>2</sub> catalyst

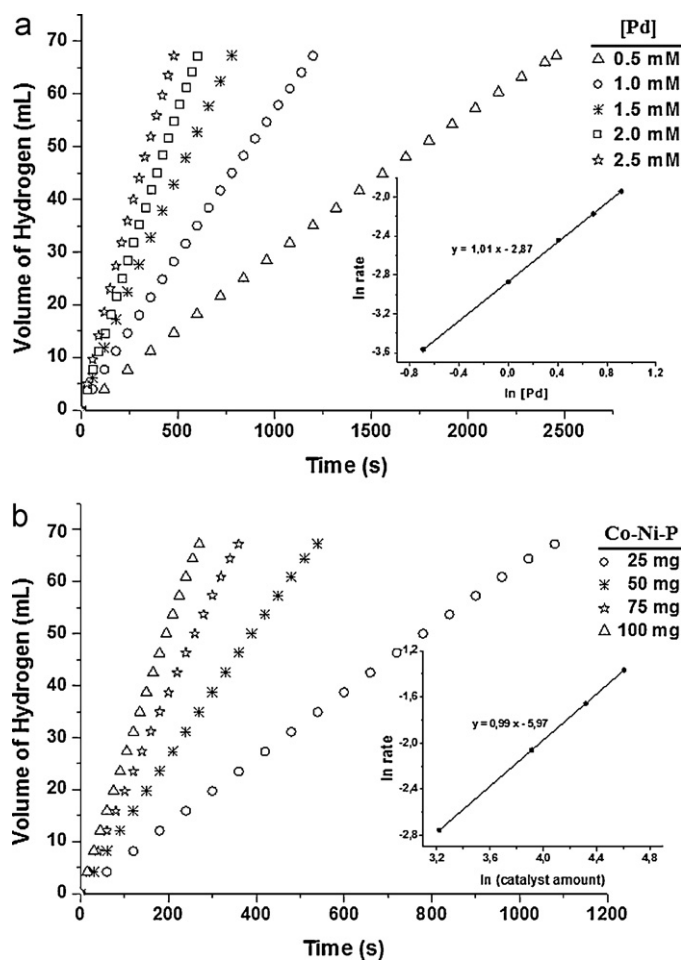
The kinetics of the hydrolysis of AB catalyzed by Pd-PVB-TiO<sub>2</sub> or Co-Ni-P/Pd-TiO<sub>2</sub> was studied by varying the catalyst concentration, substrate concentration and temperature. Before going into details on the results of the kinetic studies of the hydrolysis of stirred ammonia-borane solution, the volumes of the generated hydrogen gas under unstirred and stirred conditions in the presence of both catalysts are shown in Fig. 1 as a comparison. It is apparent from Fig. 1 that stirring has a significant effect on the overall reaction rate and thus supports the evidence of an external mass transfer resistance for the catalytic hydrolysis of AB. The choice of a stirring rate of 900 rpm was made as to eliminate the effect of mass transfer resistance in the studies. Further, with catalyst particle size range of 20–30 nm, the internal mass diffusion effects is thought to be eliminated or negligible, hence the effect of catalyst particle size was not examined since the objective of the study did not include the evaluation of the internal mass transfer resistance. Thus, the observed rate difference between unstirred and stirred conditions could be attributed to the effect of external mass transfer resistance only. It is to be noted that the volumes of generated hydrogen gas are almost 4 times higher than those obtained under unstirred conditions for both catalysts. A further appreciation of



**Fig. 2.** Hydrogen production rates ( $dH_v/dt$ ) variation with time for (a) unstirred and (b) stirred catalyst conditions.

the effect of stirring is the variation of hydrogen production rates with time for both the unstirred and stirred conditions as shown in Fig. 2. The unstirred condition shows a continuous drop in the rate of hydrogen generation throughout the experimental time period. This contrasts with the stirred condition where the generation rate remains almost constant after the end of the induction period. It is to be noted that the induction time observed resulted from non-wetting of the catalyst particles prior to the introduction of ammonia borane in the reactor. The observation is a qualitative evidence of the reaction (diffusion controlled) mechanism suggesting that as the ammonium borate byproduct is desorbed from the catalyst site, its removal from the catalyst surface is improved through stirring thereby providing constant active surface for reaction. This is unlike the unstirred case where the desorbed borate appears to cover the active site – a deactivation process similar to coking found in catalytic reactions involving hydrocarbons.

Fig. 3 shows the plots of the volume of hydrogen generated versus time during the catalytic hydrolysis of 50 mM AB solution in the presence of Pd-PVB-TiO<sub>2</sub> (Fig. 3a) or Co-Ni-P/Pd-TiO<sub>2</sub> (Fig. 3b) catalyst in different catalyst concentrations/amounts at 25 ± 0.5 °C. The hydrogen generation rate was determined from the linear portion of the plot for each experiment. The insets in Fig. 3 show the plots of the hydrogen generation rate versus initial catalyst concentration/amount, both in logarithmic scale. The slope of 1.01 ≈ 1.00 in the inset of Fig. 3a and 0.99 ≈ 1.00 in the inset of Fig. 3b indicates that hydrolysis of ammonia-borane catalyzed by Pd-PVB-TiO<sub>2</sub> or Co-Ni-P/Pd-TiO<sub>2</sub> is first order with respect to the catalyst concentration/amount. Because of the high stirring rate of 900 rpm used, the results observed for the catalyst charged amounts are viewed as the relative contributions of catalyst amount to possible mass transfer resistance to the surface reaction rate.

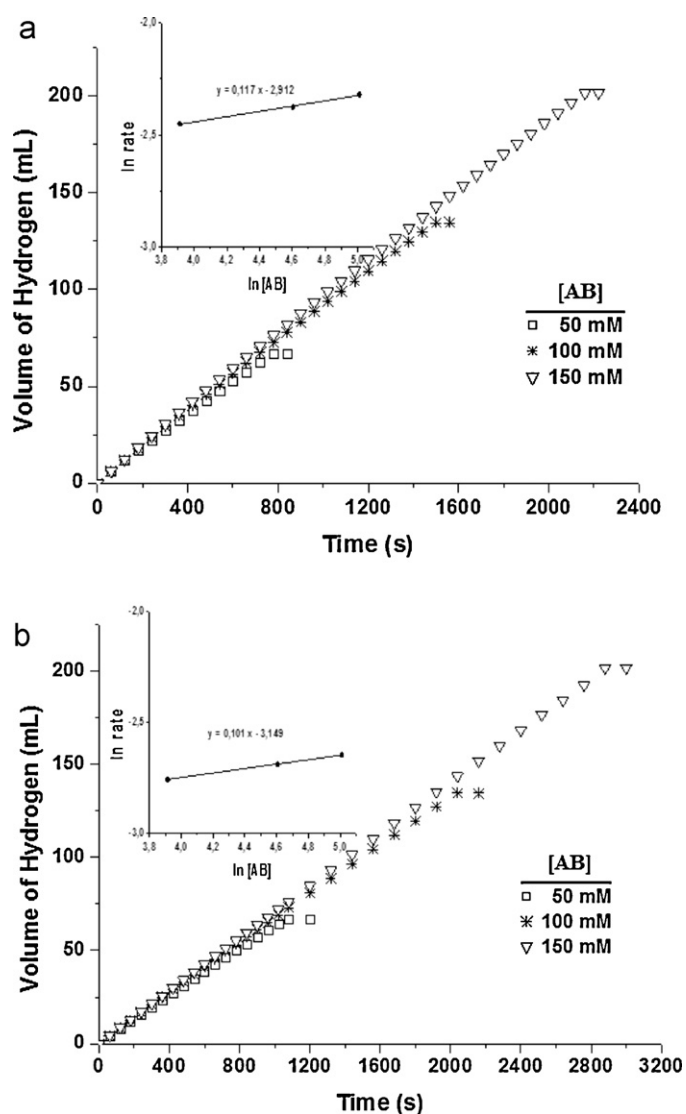


**Fig. 3.** Stirred condition volume of hydrogen versus time plots as a function of catalyst concentration/amount for (a) Pd-PVB-TiO<sub>2</sub> and (b) Co-Ni-P/Pd-TiO<sub>2</sub> catalysts for the hydrolysis of 50 mM AB at 25 ± 0.5 °C. The inset of each figure shows the plot of hydrogen generation rate versus catalyst concentration/amount (both in logarithmic scale).

The effect of H<sub>3</sub>NBH<sub>3</sub> substrate concentration on the hydrogen generation rate was also studied by carrying out a series of experiments starting with varying initial concentration of H<sub>3</sub>NBH<sub>3</sub> while keeping the catalyst concentration/amount constant at 1.5 mM Pd or 25 mg Co-Ni-P/Pd-TiO<sub>2</sub>. Fig. 4 shows the volume of hydrogen generated versus time plots as a function of the substrate concentrations at constant catalyst concentration/amount. The inset of each figure shows the plot of hydrogen generation rate versus the concentration of substrate, both in logarithmic scale, for the hydrolysis of AB for each catalyst. The hydrogen generation from the catalytic hydrolysis of ammonia-borane was found to be practically independent of AB concentration. This observation contrasts with the kinetics of the unstirred case where it was found that the hydrogen generation rate was dependent on AB concentration. The first order kinetics observed in the unstirred case is attributable to the reactant related diffusion problem over the catalyst surface caused by probable coverage of the catalyst surface by reaction by-product (ammonia metaborate) that can be eliminated through stirring [41]. Consequently, the rate law for the catalytic hydrolysis of AB catalyzed by Pd-PVB-TiO<sub>2</sub> or Co-Ni-P/Pd-TiO<sub>2</sub> catalyst under stirred condition can be given as in Eq. (2).

$$\frac{-3d[\text{NH}_3\text{BH}_3]}{dt} = \frac{d[\text{H}_2]}{dt} = k[\text{catalyst}] \quad (2)$$

Finally, Pd-PVB-TiO<sub>2</sub> or Co-Ni-P/Pd-TiO<sub>2</sub> catalyst-catalyzed hydrolysis of AB was carried out at various temperatures in



**Fig. 4.** Stirred condition volume of hydrogen versus time plots as a function of the substrate concentrations at constant catalyst concentration/amount for the hydrolysis of AB (50 mM) catalyzed by (a) Pd-PVB-TiO<sub>2</sub> (1.5 mM Pd) and (b) Co-Ni-P/Pd-TiO<sub>2</sub> (25 mg) catalysts at 25 ± 0.5 °C. The inset of each figure shows the plot of hydrogen generation rate versus the concentration of the substrate (both in logarithmic scale).

the range of 25–55 ± 0.5 °C starting with a constant initial concentration of substrate (50 mM H<sub>3</sub>NBH<sub>3</sub>) and an initial catalyst concentration/amount of 1.5 mM Pd or 25 mg Co-Ni-P/Pd-TiO<sub>2</sub>. Maximum hydrogen generation rates in the hydrolysis of AB catalyzed by the Pd-PVB-TiO<sub>2</sub> catalyst (1.5 mM) are 1910 and 14,800 mLH<sub>2</sub> min<sup>-1</sup> (g Pd)<sup>-1</sup> at 25 and 55 ± 0.5 °C, respectively. The maximum hydrogen generation rates are 170 and 1390 mLH<sub>2</sub> min<sup>-1</sup> (g catalyst)<sup>-1</sup> in the hydrolysis of AB catalyzed by Co-Ni-P/Pd-TiO<sub>2</sub> (25 mg) at 25 °C and 55 ± 0.5 °C, respectively. These maximum H<sub>2</sub> generation rates are almost 3 or 4 times higher than those obtained under unstirred conditions since they are 642 and 4367 mLH<sub>2</sub> min<sup>-1</sup> (g Pd)<sup>-1</sup> for Pd-PVB-TiO<sub>2</sub>; 60 and 400 mLH<sub>2</sub> min<sup>-1</sup> (g catalyst)<sup>-1</sup> for Co-Ni-P/TiO<sub>2</sub> at 25 °C and 55 ± 0.5 °C, respectively. The values of rate constant *k* at different temperatures (Table 1) for Pd-PVB-TiO<sub>2</sub> and Co-Ni-P/Pd-TiO<sub>2</sub> catalyst-catalyzed hydrolysis of AB were measured from the linear portions of the plots given in Fig. 5 and used for the calculation of activation energy from the Arrhenius plots shown in Fig. 6. As expected, the values of rate constants increased with the

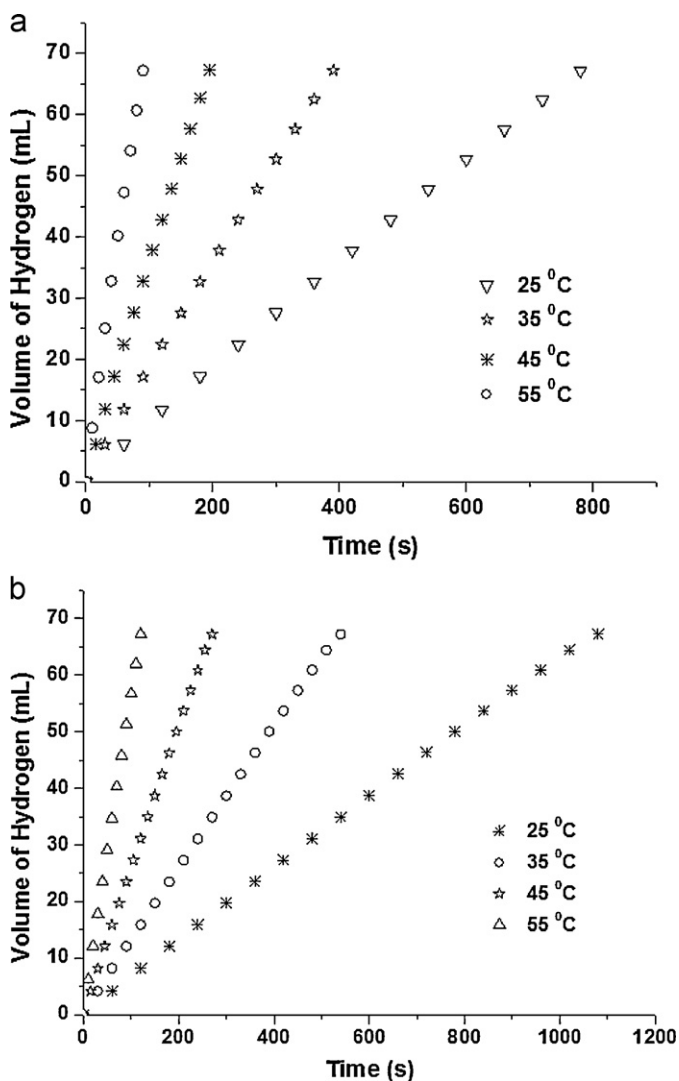


**Table 1**

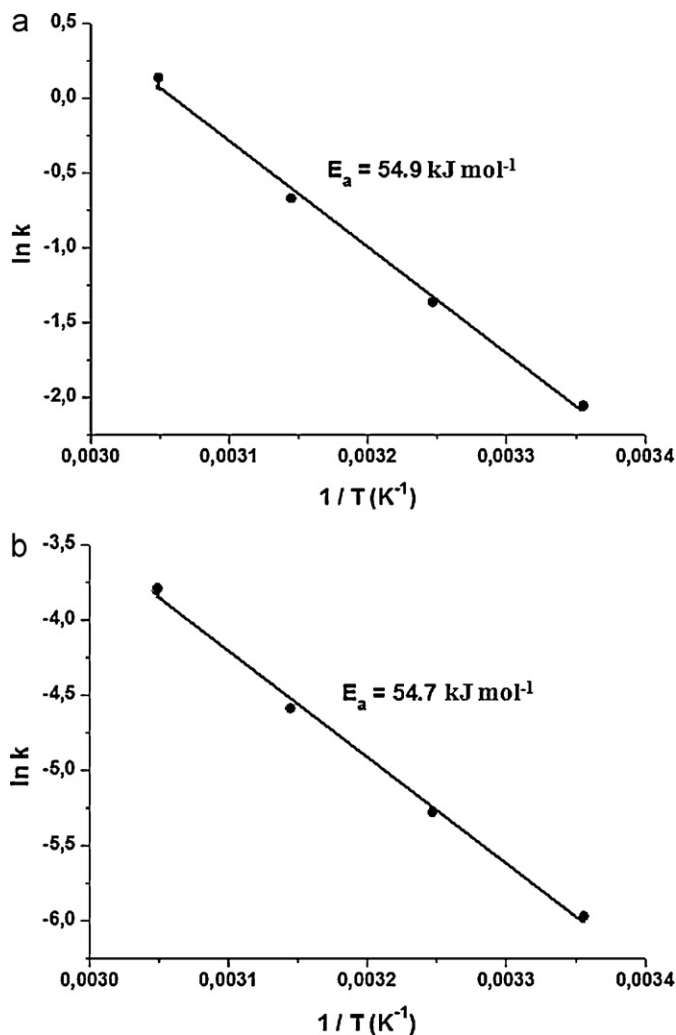
The values of rate constants  $k$  for the catalytic hydrolysis of ammonia-borane catalyzed by Pd-PVB-TiO<sub>2</sub> and Co-Ni-P/Pd-TiO<sub>2</sub> catalysts starting with a solution of 50 mM H<sub>3</sub>NBH<sub>3</sub> and 1.5 mM Pd-PVB-TiO<sub>2</sub> or 25 mg Co-Ni-P/Pd-TiO<sub>2</sub> catalyst at different temperatures.

Temperature (K)	Rate constant $k$ for Pd-PVB-TiO <sub>2</sub> (mol H <sub>2</sub> (mol Pd) <sup>-1</sup> s <sup>-1</sup> )	Rate constant $k$ for Co-Ni-P/Pd-TiO <sub>2</sub> (mL H <sub>2</sub> (mg catalyst) <sup>-1</sup> s <sup>-1</sup> )
298	0.12789	0.00255
308	0.25578	0.00510
318	0.51156	0.01018
328	1.14583	0.02263

increasing temperature. The Arrhenius activation energies were found to be 54.9 and 54.7 kJ mol<sup>-1</sup> for Pd-PVB-TiO<sub>2</sub>- and Co-Ni-P/Pd-TiO<sub>2</sub>-catalyzed hydrolysis of ammonia-borane, respectively. They are slightly lower than those found for the hydrolysis of AB using Pd-PVB-TiO<sub>2</sub> (55.9 kJ mol<sup>-1</sup>) and Co-Ni-P/Pd-TiO<sub>2</sub> (54.9 kJ mol<sup>-1</sup>) as catalysts under unstirred conditions. They are also lower than the activation energies reported in the literature for the same reaction using many different catalysts: 70 kJ mol<sup>-1</sup> for bulk nickel [45], 57 kJ mol<sup>-1</sup> for Ni<sub>0.97</sub>Pt<sub>0.03</sub> hollow spheres [31], 62 kJ mol<sup>-1</sup> for Co/γ-Al<sub>2</sub>O<sub>3</sub>



**Fig. 5.** Stirred condition volume of hydrogen versus time plots at different temperatures for the hydrolysis of AB (50 mM) catalyzed by (a) Pd-PVB-TiO<sub>2</sub> (1.5 mM Pd) and (b) Co-Ni-P/Pd-TiO<sub>2</sub> (25 mg) catalysts in the temperature range 25–55 ± 0.5 °C.



**Fig. 6.** Stirred condition Arrhenius plots for (a) Pd-PVB-TiO<sub>2</sub>- (1.5 mM Pd) and (b) Co-Ni-P/Pd-TiO<sub>2</sub> (25 mg)-catalyzed hydrolysis of AB (50 mM) at 25 ± 0.5 °C.

[2], 63 kJ mol<sup>-1</sup> for PVP-stabilized cobalt(0) nanoclusters [27], 87 kJ mol<sup>-1</sup> for K<sub>2</sub>PtCl<sub>6</sub> [11], 76 kJ mol<sup>-1</sup> for Ru/C [20], 56 kJ mol<sup>-1</sup> for zeolite confined palladium(0) nanoclusters [33]; but still higher than 23 kJ mol<sup>-1</sup> for Ru/γ-Al<sub>2</sub>O<sub>3</sub> [7], 21 kJ mol<sup>-1</sup> for Rh/γ-Al<sub>2</sub>O<sub>3</sub> [7], 21 kJ mol<sup>-1</sup> for Pt/γ-Al<sub>2</sub>O<sub>3</sub> [7], 52 kJ mol<sup>-1</sup> for Ni-Ag/C [24], 39 kJ mol<sup>-1</sup> for Pt<sub>0.65</sub>Ni<sub>0.35</sub> nanoparticles [31], 44 kJ mol<sup>-1</sup> for PSSA-co-MA stabilized Pd(0) nanoclusters [28], 44 kJ mol<sup>-1</sup> for (Co-Mo-B)/Ni foam [35], 22 kJ mol<sup>-1</sup> for Co-P catalyst [46], 52 kJ mol<sup>-1</sup> for zeolite confined copper(0) nanoclusters [32], 24 kJ mol<sup>-1</sup> for nanoparticle-assembled Co-B [38], and 47 kJ mol<sup>-1</sup> for Co-B nanospindles [37].

### 3.2. Reusability of the Pd-PVB-TiO<sub>2</sub> and Co-Ni-P/Pd-TiO<sub>2</sub> catalysts in the hydrolysis of ammonia-borane

The Pd-PVB-TiO<sub>2</sub> and Co-Ni-P/Pd-TiO<sub>2</sub> catalysts were also tested for their isolability and reusability in the hydrolysis of AB. After the complete hydrolysis of 50 mM H<sub>3</sub>NBH<sub>3</sub> solution catalyzed by 1.5 mM Pd or 25 mg Co-Ni-P/Pd-TiO<sub>2</sub> catalyst at 25 ± 0.5 °C, the catalyst was isolated as black powder, washed with water and methanol, and dried in the oven at 60 °C. The isolated samples of the Pd-PVB-TiO<sub>2</sub> and Co-Ni-P/Pd-TiO<sub>2</sub> catalysts are redispersible in aqueous solution and yet active in the hydrolysis of AB. Fig. 7 shows the conversion of AB, the percent catalytic activity of the Pd-PVB-TiO<sub>2</sub> and Co-Ni-P/Pd-TiO<sub>2</sub> catalysts

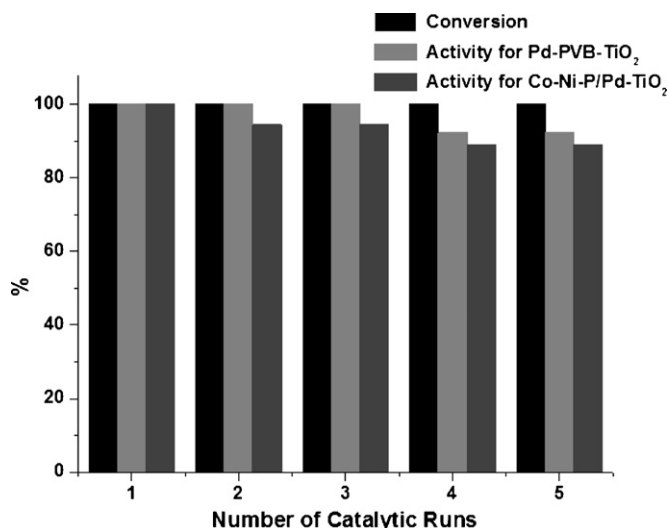


Fig. 7. % catalytic activities retained and the conversion of H<sub>3</sub>NBH<sub>3</sub> versus number of subsequent catalytic runs for Pd-PVB-TiO<sub>2</sub> (1.5 mM Pd) and Co-Ni-P/Pd-TiO<sub>2</sub> (25 mg)-catalyzed hydrolysis of AB (50 mM) at 25 ± 0.5 °C.

retained after successively repeated hydrolysis, isolation and re-dispersion cycles at 25 ± 0.5 °C. It is noteworthy that Pd-PVB-TiO<sub>2</sub> and Co-Ni-P/Pd-TiO<sub>2</sub> catalysts retain 92 and 89% of their initial activity, respectively, even at the fifth run in the hydrolysis of H<sub>3</sub>NBH<sub>3</sub> with a complete release of hydrogen. The retained initial catalytic activity values were 89 and 85% for the PVB-TiO<sub>2</sub> and Co-Ni-P/Pd-TiO<sub>2</sub> catalysts, respectively, under unstirred conditions. The slight increases in the retained catalytic activities are most probably due to the elimination of mass transfer limitation caused by lack of stirring in the unstirred cases. However, the slight decrease in catalytic activities in subsequent runs may be attributed to the passivation of the catalyst surface by increasing the concentration of boron products, e.g. metaborate, which decreases the accessibility of active sites [21,47] since the control test has shown that there is no change in the composition of catalysts. As a result, Pd-PVB-TiO<sub>2</sub> and Co-Ni-P/Pd-TiO<sub>2</sub> catalysts are isolable, redispersible and yet catalytically active in the hydrolysis of ammonia-borane.

#### 4. Conclusions

In summary, our study on the kinetics of the hydrolysis of ammonia-borane using Pd-PVB-TiO<sub>2</sub> and Co-Ni-P/Pd-TiO<sub>2</sub> catalysts under stirring conditions has led to the following conclusions and insights: under stirred conditions, the catalytic hydrolysis of AB was found to be first order with respect to catalyst concentration/amount and zero order with respect to AB concentration for both catalysts. This contrasts with the hydrolysis reactions of ammonia-borane in unstirred condition in the presence of both Pd-PVB-TiO<sub>2</sub> and Co-Ni-P/Pd-TiO<sub>2</sub> catalysts that were found to be first order with respect to AB concentration. The first order kinetics dependence on AB observed under unstirred cases is attributable to the reactant related diffusion problem over the catalysts' surface caused by metaborate by-products that cover the catalyst active site. This is a deactivation process similar to coking found in catalytic reactions involving hydrocarbons and is eliminated or reduced through stirring as demonstrated in the present work. It is found that both Pd-PVB-TiO<sub>2</sub> and Co-Ni-P/Pd-TiO<sub>2</sub> are highly active and reactivatable catalysts in the hydrolysis of AB under stirred conditions even at low concentrations and temperature. Moreover, the complete release of hydrogen is achieved even in successive runs performed by dispersing the (both) catalysts

isolated after each run. Thus, they are isolable and re-dispersible. When re-dispersed in aqueous solution of AB, Pd-PVB-TiO<sub>2</sub> and Co-Ni-P/Pd-TiO<sub>2</sub> catalysts retain 92 and 89% (These values are slightly greater than those obtained under unstirred conditions at 89 and 85%, respectively, due to the elimination of mass transfer limitation.) of their initial activity, respectively, even at the fifth run with a complete release of hydrogen. The high catalytic activity and reusability of the Pd-PVB-TiO<sub>2</sub> and Co-Ni-P/Pd-TiO<sub>2</sub> catalysts make them promising candidates to be used as catalyst in developing highly efficient portable hydrogen generation systems using AB as solid hydrogen storage material. However, the significant external mass transfer resistance observed in the unstirred condition may pose a possible challenge for possible application of the catalyst in a system without a stirring mechanism (e.g. a simple hand-held device).

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#### References

- [1] J. Turner, G. Sverdrup, K. Mann, P.G. Maness, B. Kroposki, M. Ghirardi, R.J. Evans, D. Blake, *Int. J. Energy Res.* 32 (2008) 379–407.
- [2] Q. Xu, M. Chandra, J. Power Sources 163 (2006) 364–370.
- [3] M. Chandra, Q. Xu, J. Power Sources 159 (2006) 855–860.
- [4] S.C. Amendola, S.L. Sharp-Goldman, M.S. Janjua, M.T. Kelly, P.J. Petillo, M. Binder, *J. Power Sources* 85 (2000) 186–189.
- [5] Q. Xu, M. Chandra, *J. Alloy Compd.* 446–447 (2007) 729–732.
- [6] C.L. Hsueh, C.Y. Chen, J.R. Ku, S.F. Tsai, Y.Y. Hsu, F. Tsau, M.S. Jeng, *J. Power Sources* 177 (2008) 485–492.
- [7] M. Chandra, Q. Xu, *J. Power Sources* 168 (2007) 135–142.
- [8] W. Grochala, P.P. Edwards, *Chem. Rev.* 104 (2004) 1283–1316.
- [9] J.A. Rood, B.C. Noll, K.W. Henderson, *Inorg. Chem.* 45 (2006) 5521–5528.
- [10] F.H. Stephens, V. Pons, R.T. Baker, *Dalton Trans.* 25 (2007) 2613–2626.
- [11] N. Mohajeri, A. T-Raissi, O. Adebisi, *J. Power Sources* 167 (2007) 482–485.
- [12] A.C. Stowe, W.J. Shaw, J.C. Linehan, B. Schmid, T. Autrey, *Phys. Chem. Chem. Phys.* 9 (2007) 1831–1836.
- [13] T. Umegaki, J.M. Yan, X.B. Zhang, H. Shioyama, N. Kuriyama, Q. Xu, *Int. J. Hydrogen Energy* 34 (2008) 2303–2311.
- [14] Basic Research Needs For the Hydrogen Economy, Report of the Basic Energy Sciences Workshop on Hydrogen Production, Storage and Use, May 13–15, 2003, Office of Science, U.S. Department of Energy, [www.sc.doe.gov/bes/hydrogen.pdf](http://www.sc.doe.gov/bes/hydrogen.pdf).
- [15] Annual Energy Outlook 2005 With Projections To 2025, Energy Information Administration, February 2005, [www.eia.doe.gov/oiaf/aeo/pdf/0383\(2005\).pdf](http://www.eia.doe.gov/oiaf/aeo/pdf/0383(2005).pdf).
- [16] K.S. Eom, M. Kim, R.H. Kim, D.H. Nam, H.S. Kwon, *J. Power Sources* 195 (2010) 2830–2834.
- [17] J.M. Yan, X.B. Zhang, S. Han, H. Shioyama, Q. Xu, *J. Power Sources* 194 (2009) 478–481.
- [18] P.V. Ramachandran, P. Gagare, *Inorg. Chem.* 46 (2007) 7810–7817.
- [19] F. Cheng, H. Ma, Y. Li, J. Chen, *Inorg. Chem.* 46 (2007) 788–794.
- [20] S. Basu, A. Brockman, P. Gagare, Y. Zheng, P.V. Ramachandran, W.N. Delgass, *J. Power Sources* 188 (2009) 238–243.
- [21] T.J. Clark, G.R. Whittell, I. Manners, *Inorg. Chem.* 46 (2007) 7522–7527.
- [22] S.B. Kalidindi, U. Sanyal, B.R. Jagirdar, *Phys. Chem. Chem. Phys.* 10 (2008) 5870–5874.
- [23] T. Umegaki, J.M. Yan, X.B. Zhang, H. Shioyama, N. Kuriyama, Q. Xu, *J. Power Sources* 191 (2009) 209–216.
- [24] C.F. Yao, L. Zhuang, Y.L. Cao, X.P. Hi, H.X. Yang, *Int. J. Hydrogen Energy* 33 (2008) 2462–2467.
- [25] J.M. Yan, X.B. Zhang, S. Han, H. Shioyama, Q. Xu, *Angew. Chem., Int. Ed.* 47 (2008) 2287–2289.
- [26] T. Umegaki, J.M. Yan, X.B. Zhang, H. Shioyama, N. Kuriyama, Q. Xu, *Int. J. Hydrogen Energy* 34 (2009) 3816–3822.
- [27] Ö. Metin, S. Özkar, *Energy Fuels* 23 (2009) 3517–3526.
- [28] Ö. Metin, Ş. Şahin, S. Özkar, *Int. J. Hydrogen Energy* 34 (2009) 6304–6313.
- [29] J.M. Yan, X.B. Zhang, H. Shioyama, Q. Xu, *J. Power Sources* 195 (2010) 1091–1094.
- [30] J.M. Yan, X.B. Zhang, S. Han, H. Shioyama, Q. Xu, *Inorg. Chem.* 48 (2009) 7389–7393.
- [31] X. Yang, F. Cheng, J. Liang, Z. Tao, J. Chen, *Int. J. Hydrogen Energy* 34 (2009) 8785–8791.

- [32] M. Zahmakıran, F. Durap, S. Özkar, *Int. J. Hydrogen Energy* 35 (2010) 187–197.
- [33] M. Rakap, S. Özkar, *Int. J. Hydrogen Energy* 35 (2010) 1305–1312.
- [34] M. Rakap, S. Özkar, *Int. J. Hydrogen Energy* 35 (2010) 3341–3346.
- [35] M. Zahmakıran, T. Ayvalı, S. Akbayrak, S. Çalışkan, D. Çelik, S. Özkar, *Catal. Today* 170 (2011) 76–84.
- [36] H.B. Dai, L.L. Gao, Y. Liang, X.D. Kang, P. Wang, *J. Power Sources* 195 (2010) 307–312.
- [37] D.G. Tong, X.L. Zeng, W. Chu, D. Wang, P. Wu, *J. Mater. Sci.* 45 (2010) 2862–2867.
- [38] N. Patel, R. Fernandes, G. Guella, A. Miotello, *Appl. Catal. B* 95 (2010) 137–143.
- [39] H.L. Jiang, T. Umegaki, T. Akita, X.B. Zhang, M. Haruta, Q. Xu, *Chem. Eur. J.* 16 (2010) 3132–3137.
- [40] Y. Yamada, K. Yano, Q. Xu, S. Fukuzumi, *J. Phys. Chem. C* 114 (2010) 16456–16462.
- [41] M. Rakap, E.E. Kalu, S. Özkar, *Int. J. Hydrogen Energy* 36 (2011) 254–261.
- [42] M. Rakap, E.E. Kalu, S. Özkar, *Int. J. Hydrogen Energy* 36 (2011) 1448–1455.
- [43] Ö. Metin, S. Özkar, S. Sun, *Nano Res.* 3 (2010) 767–784.
- [44] T. Umegaki, J.M. Yan, X.B. Zhang, H. Shioyama, N. Kuriyama, Q. Xu, *J. Power Sources* 195 (2010) 8209–8214.
- [45] S.B. Kalidindi, M. Indirani, B.R. Jagirdar, *Inorg. Chem.* 47 (2008) 7424–7429.
- [46] K.S. Eom, K.W. Cho, H.S. Kwon, *Int. J. Hydrogen Energy* 35 (2010) 181–186.
- [47] C.A. Jaska, T.J. Clark, S.B. Clendenning, D. Groeza, A. Turak, Z.H. Lu, I. Manners, *J. Am. Chem. Soc.* 127 (2005) 5116–5124.