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# Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

Short communication

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# Palladium on carbon as an efficient, durable and economical catalyst for the alcoholysis of $B_2pin_2$



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ARTICLE INFO

Keywords: Pd/C B<sub>2</sub>pin<sub>2</sub> Alcoholysis H<sub>2</sub> Tandem reaction

#### ABSTRACT

Hydrogen has attracted much attention as one of the most promising chemical fuel candidates because of its zero emission during consumption. In order to solve the freezing problem of water based hydrolysis process, herein, the Pd/C as an efficient and stable catalyst for the methanolysis, ethanolysis, propanolysis and butanolysis of B<sub>2</sub>pin<sub>2</sub> for the generation of hydrogen has been first developed. The large kinetic isotope effect (KIE) of k<sub>H</sub>/k<sub>D</sub> = 5.0, D<sub>2</sub> formation from CD<sub>3</sub>OD and *in situ* tandem reaction have confirmed that alcohol is the only hydrogen source. Interestingly, the order of  $E_a$  of these alcohols in H<sub>2</sub> evolution is MeOH (methanol, 29.57 kJ/mol) < EtOH (ethanol, 34.80 kJ/mol) < PrOH (propanol, 39.08 kJ/mol) < <sup>n</sup>BuOH (n-butanol, 41.98 kJ/mol), which is consistent with the known order of acidities of these alcohols (MeOH > EtOH > PrOH > <sup>n</sup>BuOH).

# 1. Introduction

The 21st century,  $H_2$  has been regarded as one of the most promising alternatives to fossil fuels due to its high energy density, sustainability and zero pollution [1–5]. So, a large deal of researches have been devoted to  $H_2$  evolution upon the hydrolysis of various hydrogen storage materials, such as dimethylamine-borane, sodium borohydride, hydrazine borane, hydrazine hydrate, formic acid and ammonia borane [6–18]. However, it is still a challenge to develop the hydrolysis of hydrogen storage materials at subzero temperature (the freezing point of water is only 0 °C).

Recently, the H<sub>2</sub> evolution upon alcoholysis of hydrogen storage materials have attracted considerable attention, because it perfectly solves the freezing problem of water based hydrolysis process [12,19–24]. In general, NH<sub>3</sub> is released along with H<sub>2</sub> gas in the hydrolysis of hydrogen storage materials. Whereas NH<sub>3</sub> is not released in the alcoholysis of hydrogen storage materials [25–26], thus pure H<sub>2</sub> is formed. Furthermore, the by-products of alcoholysis reaction, such as NH<sub>4</sub>B(OCH<sub>3</sub>)<sub>4</sub> and NaB(OCH<sub>3</sub>)<sub>4</sub>, can be easily reconverted into hydrogen storage materials by reaction with LiAlH<sub>4</sub> and NH<sub>4</sub>Cl [27]. Among them, alcoholysis of  $NH_3BH_3$ ,  $NaBH_4$  or related boron compounds producing  $H_2$  with only one H atom provided by alcohol and the other one by boron compounds [28–32].

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In fact, our group has a long term active interest in the exploration of new H<sub>2</sub> evolution system [33]. For example, in 2020, our group reported the H<sub>2</sub> evolution upon hydrolysis of tetrahydroxydiboron catalyzed by graphene quantum dot-stabilized transition metal nanoparticles, in which both atoms of H<sub>2</sub> evolution are provided by H<sub>2</sub>O [33a]. Herein, we report Pd/C-catalyzed H<sub>2</sub> or D<sub>2</sub> evolution from alcoholysis of B<sub>2</sub>pin<sub>2</sub>, in which both two H atoms are obtained from alcohols (including MeOH, EtOH, PrOH, and <sup>n</sup>BuOH (**Eq. (1**)). Among them, B<sub>2</sub>pin<sub>2</sub> is typically used as a current borylation source [34–38], and rarely applied in the reduction reactions [39–41]. According to our knowledge, it is the first systematic research of H<sub>2</sub> evolution from the alcoholysis of B<sub>2</sub>pin<sub>2</sub>, although Prabhu and Stoke mentioned that H<sub>2</sub> gas could be released

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https://doi.org/10.1016/j.inoche.2021.108732

Received 10 April 2021; Received in revised form 31 May 2021; Accepted 31 May 2021 Available online 10 June 2021 1387-7003/© 2021 Elsevier B.V. All rights reserved.

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Fig. 1. (a) TEM image of Pd/C obtained at 200 kV voltage; (b) XRD of Pd/C.



Fig. 2. (a) Comparison of the evolution of H<sub>2</sub> from alcoholysis of B<sub>2</sub>pin<sub>2</sub> catalyzed by 6 mol‰ Pd/C; (b) The initial TOF comparison about different alcoholysis at 40% conversion.

from  $B_2pin_2$  and MeOH [42]. In addition, Pd/C, as a commercial, cheap and heterogeneous catalyst [43], has been successfully recycled 5 times for  $H_2$  evolution without any activity loss by the simple filtration.

# 2. Material and methods

# 2.1. Chemicals and reagents

All commercial materials were used without further purification, unless indicated. The deionized water was prepared in the laboratory. MeOH, EtOH, PrOH, <sup>n</sup>BuOH were purchased from Saen Chemical Technology (Shanghai) Co., Ltd. B<sub>2</sub>Pin<sub>2</sub> was purchased from Shanghai McLin Biochemical Technology Co., Ltd; CD<sub>3</sub>OD, Pd/C, norbornene and were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China, http://www.aladdin-e.com/).

#### 2.2. Pd/C catalyzed $H_2$ evolution

As a conventional method, the methanolysis of  $B_2pin_2$  was executed in MeOH at 303 K. Further details,  $B_2pin_2$  (0.5 mmol) and 2–8 mol‰ of Pd/C were added into a 10 mL round bottom flask. Then, 5 mL MeOH was injected and stopwatch was opened. The hydrogen volume was recorded periodically by a water-filled gas burette through displacement of water. A quantitative conversion of  $B_2pin_2$  produced 1.0equivalents of H<sub>2</sub>, and occupied ca. 22.4 mL at atmospheric pressure. Prior to the reactions, the volumes were measured at atmospheric pressure and corrected for water vapor pressure at room temperature.

#### 3. Results and discussion

Firstly, the commercial Pd/C has been measured by transmission electron microscope (TEM), the size of Pd/C is 3.29 nm (Fig. 1a and S1). The X-ray diffraction (XRD) of Pd/C has also been recored in the Fig. 1b. It shows a typical profile with a broad peak at around 24° corresponding to the C (002) peak (JCPDS Card No, 75-0444). While the peaks at 40.01°, 46.53° and 67.92° are belonged to (111), (200) and (220) of Pd (JCPDS Card No, 88-2335). The commercial Pd/C has been acted as catalysts for the H<sub>2</sub> generation from the alcoholysis of the B<sub>2</sub>pin<sub>2</sub>. The evolution of H<sub>2</sub> upon reaction between B<sub>2</sub>pin<sub>2</sub> and alcohol (including MeOH, EtOH, PrOH, and <sup>n</sup>BuOH) catalyzed by 6 mol‰ Pd/C was conducted at 30 °C and atmospheric pressure. The volume of produced H<sub>2</sub> gas has been monitored by water displacement via a gas burette. For all the results with different alcohols shown in Fig. 2a, it is clear that 1 mmol of H<sub>2</sub> gas was provided from 1 mmol of B<sub>2</sub>pin<sub>2</sub> and the order of reaction rate constant of these alcohols in H<sub>2</sub> evolution is MeOH > EtOH > PrOH > <sup>n</sup>BuOH (Fig. 2b). Among them, methanolysis of B<sub>2</sub>pin<sub>2</sub> presents the highest TOF of 220.21 mol(H<sub>2</sub>)·mol<sub>Pd</sub><sup>-1</sup>·min<sup>-1</sup>.

In order to obtain the kinetic data of methanolysis of B<sub>2</sub>pin<sub>2</sub>, the effects of concentrations of Pd/C and B<sub>2</sub>pin<sub>2</sub>, and reaction temperature have been investigated in the Fig. 3. The Fig. 3a shows the time plots of the catalytic H<sub>2</sub> evolution upon methanolysis of B<sub>2</sub>pin<sub>2</sub> in the presenct of various amount of Pd/C, we find Pd/C follows first-order reaction kinetics as a function of catalyst amount (Fig. 3b). The H<sub>2</sub> evolution upon methanolysis of B<sub>2</sub>pin<sub>2</sub> (from 0.25 to 1 mmol) in the presence of 0.002 mol of Pd/C (Fig. 3c). The methanolysis of B<sub>2</sub>pin<sub>2</sub> is also first-order reaction kinetics as a function of B<sub>2</sub>pin<sub>2</sub> amount (Fig. 3d). The Activation energy ( $E_a$ ) is the minimum energy required to start a chemical reaction, and it has



**Fig. 3.** (a) Time plots of the catalytic  $H_2$  evolution upon methanolysis of  $B_2pin_2$  by various amount of Pd/C; (b) Plots of the rates of  $H_2$  generation vs. the amount of the Pd/C, both on natural logarithmic scale. (c) Plots of the volume of hydrogen generated vs. time for methanolysis of  $B_2pin_2$  catalyzed by 0.002 mmol of Pd/C (5% w/w) at various amount of  $B_2pin_2$ ; (d) and the plot of hydrogen generation rate versus the concentration of  $B_2pin_2$  both in natural logarithmic scale. (e) Plots of volume of  $H_2$  vs. time for the 2 mol‰ of Pd/C catalyzed methanolysis of  $B_2pin_2$  at different temperatures; (f) Arrhenius plots obtained from the kinetic data.

been widely used for evaluation of catalyst. Then the H<sub>2</sub> evolution upon methanolysis of B<sub>2</sub>pin<sub>2</sub> have been carried out at different temperatures (from 298 to 313 K) in the Fig. 3e, and the k values are corrected by an Arrhenius-type expression:  $Lnk = LnA - \frac{E_a}{RT}$ , where  $E_a$ , the activation energy (kJ/mol) and A, the pre-exponential factor (min<sup>-1</sup>), are deduced using the plot of Ln k to the 1/T depicted in the Fig. 3f. The  $E_a$  of the Pd/ C has been calculated to be 29.57 kJ/mol. In parallel, in order to obtain the kinetic data of ethanolysis (Fig. 4), propanolysis (Fig. 5) and butanolysis (Fig. 6) of B<sub>2</sub>pin<sub>2</sub>, the effects of concentrations of Pd/C and B<sub>2</sub>pin<sub>2</sub>, and reaction temperature have also been investigated. The activation energy  $(E_a)$  of the Pd/C catalyzed H<sub>2</sub> evolution upon ethanolysis (Fig. 4f), propanolysis (Fig. 5f) and butanolysis (Fig. 6f) of B<sub>2</sub>pin<sub>2</sub> has been calculated to be 34.80 kJ/mol, 39.08 kJ/mol and 41.98 kJ/ mol, respectviely. Interestingly, the order of activation energy constant of these alcohols in H<sub>2</sub> evolution is MeOH < EtOH < PrOH < <sup>n</sup>BuOH, which is consistent with the order of acidities of these alcohols in H<sub>2</sub> evolution. Then, the kinetic isotope effect (KIE) using CD<sub>3</sub>OD instead of CH<sub>3</sub>OH for methanolysis of B<sub>2</sub>pin<sub>2</sub> has been investigated in the Fig. **7a**. A large KIE of  $k_H/k_D = 5.0$  is obtained, suggesting that the O-H bond cleavage of methanol is the rate-determining step of H<sub>2</sub> evolution. In summary, the order of activation energy constant of these alcohols indicates that, consistent with the known order of actidities of these alcohols resulting from the rate limiting O-H activation step, the most actidic alcohol MeOH are the most active one.

In addition, the H<sub>2</sub> evolution upon methanolysis of B<sub>2</sub>pin<sub>2</sub> catalyzed by 0.5 mol% Pd/C has been carred out at -15 °C, Fig. 7b shows that the H<sub>2</sub> evolution still works well. It is clear that the H<sub>2</sub> evolution upon alcoholysis of B<sub>2</sub>pin<sub>2</sub> could solve the freezing problem of water based hydrolysis process at subzero temperature.

The reusability of the Pd/C catalyst has also been tested in the methanolysis of  $B_2pin_2$  (Fig. 8a). The Pd/C catalyst was re-obtained and reused by filtration, washing and drying after each  $H_2$  evolution. It is



**Fig. 4.** (a) Time plots of the catalytic  $H_2$  evolution upon ethanolysis of  $B_2pin_2$  by various amount of Pd/C; (b) Plots of the rates of  $H_2$  generation vs. the amount of the Pd/C, both on natural logarithmic scale. (c) Plots of the volume of hydrogen generated vs. time for ethanolysis of  $B_2pin_2$  catalyzed by 0.002 mmol of Pd/C (5% w/w) at various amount of  $B_2pin_2$ ; (d) and the plot of hydrogen generation rate versus the concentration of  $B_2pin_2$  both in natural logarithmic scale. (e) Plots of volume of  $H_2$  vs. time for the 4 mol‰ of Pd/C catalyzed ethanolysis of  $B_2pin_2$  at different temperatures; (f) Arrhenius plots obtained from the kinetic data.

obvious that the hydrogen generation rate is mostly constant even after 5 times cycles. After the 5th catalyst recycling, in the Fig. 8b, the TEM shows the size of Pd/C (3.31 nm) remains unchanged (Fig. S2), which is indicative of stable catalytic activity and good recyclability of Pd/C in the methanolysis of B<sub>2</sub>pin<sub>2</sub>.

After studying Pd/C catalyzed  $H_2$  evolution upon alcoholysis of  $B_2pin_2$ , we next investigate the tandem catalysis by using *in situ* generated  $H_2$  upon methanolysis of  $B_2pin_2$  for hydrogenation of norbornene in a sealed two-chamber system (**Scheme S1**). The result exhibits that the norbornene hydrogenation provided 99% yield of the desired products after 12 h at 30 °C (**Eq. (2)**), confirming the evolution of  $H_2$  upon the reaction of  $B_2pin_2$  and CH<sub>3</sub>OH. For the hydrogenation of norbornene with  $D_2$ , which is *in situ* generated from the reaction of  $B_2pin_2$  and CD<sub>3</sub>OD, the desired product **2b** is also obtained in 99% yield (**Eq. (3)**). This suggests both two H atoms of  $H_2$  gas are provided by MeOH, rather than one H atom by MeOH and the other one by boron compounds [7].

Based on our previous work [33a], a conjectural mechanism of Pd/C catalyzed  $H_2$  evolution upon alcoholysis of  $B_2pin_2$  has been proposed in the Fig. 9. First,  $B_2pin_2$  reacts with Pd/C to form intermediate I, subsequently transformed to intermediate II after the attack of alcoholysis (ROH) molecules. Finally, a dihydride Pd(H)<sub>2</sub> species III is produced from II by releasing two molecule of BpinOR, simultaneously affording



**Fig. 5.** (a) Time plots of the catalytic  $H_2$  evolution upon propanolysis of  $B_2pin_2$  by various amount of Pd/C; (b) Plots of the rates of  $H_2$  generation vs. the amount of the Pd/C, both on natural logarithmic scale. (c) Plots of the volume of hydrogen generated vs. time for propanolysis of  $B_2pin_2$  catalyzed by 0.004 mmol of Pd/C (5% w/w) at various amount of  $B_2pin_2$ ; (d) and the plot of hydrogen generation rate versus the concentration of  $B_2pin_2$  both in natural logarithmic scale. (e) Plots of volume of  $H_2$  vs. time for the 8 mol‰ of Pd/C catalyzed propanolysis of  $B_2pin_2$  at different temperatures; (f) Arrhenius plots obtained from the kinetic data.

 $H_2$ .

# 4. Conclusion

In summary, the Pd/C has been first developed as an efficient and stable catalyst for the methanolysis, ethanolysis, propanolysis and butanolysis of B<sub>2</sub>pin<sub>2</sub> for the generation of hydrogen. This method is found to be facile, scalable and economical. The commercial Pd/C catalyst exhibits high catalytic activity for the alcoholysis of B<sub>2</sub>pin<sub>2</sub>, which is typically used as a current borylation source. The large KIE of  $k_H/k_D = 5.0$  using CD<sub>3</sub>OD instead of CH<sub>3</sub>OH for methanolysis of B<sub>2</sub>pin<sub>2</sub> and tandem reaction for hydrogenation of norbornene have confirmed both two H atoms of H<sub>2</sub> gas are provided from CH<sub>3</sub>OH. Interestingly, the order of E<sub>a</sub> of these alcohols in H<sub>2</sub> evolution is MeOH (29.57 kJ/mol) < EtOH (34.80 kJ/mol) < PrOH (39.08 kJ/mol) < <sup>n</sup>BuOH (41.98 kJ/mol), which is consistent with the known order of acidities of these alcohols (MeOH > EtOH > PrOH > <sup>n</sup>BuOH) and resulting from the rate limiting O-H activation step. So the most acidic MeOH is the most active one. Moreover, It is clear that the H<sub>2</sub> evolution upon methanolysis of B<sub>2</sub>pin<sub>2</sub>

(at -15 °C) could solve the freezing problem of water based hydrolysis process at subzero temperature. In addition, Pd/C catalyst could be easily separated and re-obtained from reaction with excellent stability amd catalytic activity.

# CRediT authorship contribution statement

Junjie Zhou and Ning Li: Data curation, Formal analysis, Investigation, Methodology. Jialu Shen: Formal analysis. Xu Meng and Xiang Liu: Funding acquisition, Project administration, Resources, Software, Supervision, Validation, Visualization, Writing - original draft, Writing review & editing.

# **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.



**Fig. 6.** (a) Time plots of the catalytic  $H_2$  evolution upon butanolysis of  $B_2pin_2$  by various amount of Pd/C; (b) Plots of the rates of  $H_2$  generation vs. the amount of the Pd/C, both on natural logarithmic scale. (c) Plots of the volume of hydrogen generated vs. time for butanolysis of  $B_2pin_2$  catalyzed by 0.004 mmol of Pd/C (5% w/w) at various amount of  $B_2pin_2$ ; (d) and the plot of hydrogen generation rate versus the concentration of  $B_2pin_2$  both in natural logarithmic scale. (e) Plots of volume of  $H_2$  vs. time for the 8 mol‰ of Pd/C catalyzed butanolysis of  $B_2pin_2$  at different temperatures; (f) Arrhenius plots obtained from the kinetic data.



Fig. 7. (a) Hydrogen evolution from  $B_2pin_2$  with  $CH_3OH$  and  $CD_3OD$ ; (b) The Time plots of the catalytic  $H_2$  evolution upon methanolysis of  $B_2pin_2$  catalyzed by 0.5 mol% Pd/C at -15 °C.



Fig. 8. (a) The B<sub>2</sub>pin<sub>2</sub> methanolysis with 4 mol‰ Pd/C during the reusability test. (b) TEM image of 5th used Pd/C.



Fig. 9. Proposed mechanism of H<sub>2</sub> evolution upon B<sub>2</sub>pin<sub>2</sub> alcoholysis.

### Acknowledgement

Financial support from the National Natural Science Foundation of China (21805166), the 111 Project (D20015), the Engineering Research Center of Eco-environment in Three Gorges Reservoir Region, Ministry of Education, China Three Gorges University (KF2019-05), the outstanding young and middle-aged science and technology innovation teams, Ministry of Education, Hubei province, China (T2020004), Foundation of Science and Technology Bureau of Yichang City (A21-3-012) the Youth Innovation Promotion Association CAS (2018456) and LICP Cooperation Foundation for Young Scholars (HZJJ20-10) is gratefully acknowledged.

### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi. org/10.1016/j.inoche.2021.108732.

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