

Hydrolysis of B₂pin₂ over Pd/C Catalyst: High Efficiency, Mechanism, and *in situ* Tandem Reaction

Ning Li^{+,[a]} Jialu Shen^{+,[a]} and Xiang Liu^{*[a]}

A facile and effective synthesis of H_2 or D_2 from Pd/C catalyzed hydrolysis of B_2pin_2 has first been developed. Among them, B_2pin_2 is frequently used for borylation reaction, and has rarely been used for hydrogen evolution. The kinetic isotope effects (KIEs) and tandem reaction for diphenylacetylene and norbornene hydrogenation have confirmed both two H atoms of H_2 gas are provided from H_2O . This is contrary to other boron compounds hydrolysis (including NH_3BH_3 , $NaBH_4$), which generates H_2 with only one H atom provided by water and the other one by boron compounds. Note that the hydrolysis of B_2pin_2 in D_2O also provides an easy and useful synthesis of D_2 .

Introduction

Over the past two decades, it has become an significant mainstream in the world to explore clean and renewable energy, due to the ever-increasing of the depletion of non-renewable fossil resources (including natural gas, oil and coal) and the crazy development of global economy.^[1–4] Among all kinds of renewable energy resources, hydrogen is regarded as one of the most potential alternative source with high chemical energy (142 MJ/kg) due to its clean, abundant, efficient and sustainable characteristics.^[5–7] However, the safe production, storage and transport of H₂ is still a challenging task. As H₂ is in the form of gas at normal atmospheric pressure and needs low temperature to be liquefied H₂ (70 g/L at 20 K) or high pressure to be converted to compressed H₂ (40 g/L at 700 bar), which limits the development of hydrogen energy technology.^[8,9]

Recently, catalytic hydrolysis of hydrogen storage materials (such as borohydrides, organic compounds and metal hydrides) has attracted more and more attention, because it is a safe, facile and efficient method for producing, transporting and storing hydrogen.^[10-17] Typically, B₂pin₂ (bis(pinacolato)diboron) is often applied as a current borylation source,^[18-22] and it has rarely been used for reduction reactions.^[23-26] For example, in 2016, Pd(OAc)₂-catalyzed transfer hydrogenation of N-heteroaromatics *via* a combined B₂pin₂/H₂O system, had been reported

[a] N. Li,⁺ J. Shen,⁺ Prof. Dr. X. Liu
 College of Materials and Chemical Engineering,
 Key Laboratory of Inorganic Nonmetallic Crystalline and Energy Conversion
 Materials,
 Analysis and Testing Center, China Three Gorges University,
 Yichang, Hubei 443002, China

E-mail: xiang.liu@ctgu.edu.cn

[⁺] These authors are contributed equally to this work and should be considered as co-first authors.

Supporting information for this article is available on the WWW under https://doi.org/10.1002/ejic.202001132 by Song's group (Scheme 1a).^[27] In 2016, Prabhu's group further confirmed that clean hydrogen gas is produced from water by Pd(OAc)₂-catalyzed hydrolysis of B₂pin₂ (Scheme 1b).^[28,29] In 2019, with a combined ethanol/B₂pin₂ system as the hydrogen source, Jin and Liu's group also reported CuCl/Ligand-catalyzed semihydro-genation of alkynes to synthesize Z-alkenes with excellent stereoselectivity (Scheme 1c).^[30] As a part of our current studies on the development of new hydrogen storage materials and new catalytic system for H₂ evolution,^[31] herein, we first report Pd/C as an efficient and reusable catalyst for H₂ evolution from the hydrolysis of B₂pin₂ (Scheme 1d). To our knowledge, this is the first systematic study of hydrogen evolution from the hydrolysis of B₂pin₂, although Prabhu's group and Nielsen and Skrydstrup's group mentioned H₂ evolution from the hydrolysis of B₂pin₂.^[25,28] Among them, Pd/C is a very cheap and commercial source of palladium,^[32] it shows efficient catalytic activity in the H₂ evolution even without ligands. We found Pd/C, as a heterogeneous catalyst, has been successfully recycled 5 times without any activity loss for H₂ evolution by the simple filtration. In addition, kinetic isotope effects (KIEs) and tandem reaction for diphenylacetylene and norbornene hydrogenation have also been investigated for the mechanism study of the B₂pin₂ hydrolysis.

> (a) Song's work Pd(OAc)₂, B₂pin₂ H₂O, w/o base, (b) Prabhu's work [Pd(OAc)₂]₃, PCy₃ R^2 (c) Jin and Liu's work -R² CuCl/Ligand, *t*-BuOK B₂pin₂, EtOH, r.t (d) This work Pd/C B₂pin₂ + D_2O (Bpin)₂O In situ Pd/C

Scheme 1. B₂Pin₂-Assisted Transfer Hydrogenation Reactions

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Results and Discussion

First, the size of Pd/C is 3.29 nm, confirmed by transmission electron microscopy (TEM) in the Figure 1. The B_2pin_2 hydrolysis catalyzed by various amount of Pd/C (from 0.2 mol% to 1.0 mol%) have been conducted at 30 °C (Eq. 1). The plots of the hydrogen volume *vs.* time for various amounts of Pd/C has been shown in Figure 2a. The Figure 2b represents that the



Figure 1. (a) The TEM of Pd/C; (b). Distribution diagram of Pd/C.



Figure 2. (a) Time plots of the catalytic evolution of H_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.



Figure 3. (a) Plots of the volume of hydrogen generated vs. time for the evolution of H₂ catalyzed by 4 mol‰ Pd/C at various amount of B₂pin₂; (b) and the plot of hydrogen generation rate versus the concentration of B₂pin₂ both in natural logarithmic scale.



Figure 4. (a) Plots of volume of H_2 vs. time for the 0.4 mol% of Pd/C catalyzed hydrolysis of B_2pin_2 at different temperatures; (b) Arrhenius plots obtained from the kinetic data.

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slope of the logarithmic plot of the H₂ evolution rate and the Pd/C concentration is 0.80, indicating that the generation rate of H₂ is first-order in Pd/C concentration. At the same time, The Figure 3 exhibits that the plot of H₂ generation *vs.* concentration of B₂pin₂ is 0.70, showing the activation of B₂pin₂ is also first-order. Then the time dependence of H₂ generation at various temperatures (from 298 K to 313 K) has been investigated in the Figure 4a. The activation energy is 25.65 KJ/mol for Pd/C based on the Arrhenius equation (Figure 4b).

Our previous work has demonstrated that both of the hydrogen atoms in H₂ comes from water for the metal-catalyzed B₂(OH)₄ hydrolysis, and kinetic isotope effect (KIE) has confirmed that the O–H bond cleavage of H₂O is the rate-determining step.^[31] Here, the KIE using D₂O instead of H₂O for Pd/C catalyzed H₂ evolution upon B₂pin₂ hydrolysis has also been investigated. Indeed, the KIE value found for the present reaction (Figure 5) including the B₂pin₂/D₂O system, k_H/k_D= 3.26, is very high and represents a primary KIE, confirming that the O–H bond cleavage of H₂O is the rate-determining step.

The durability of Pd/C catalyst has been investigated due to its importance for practical applications (Figure 6). Pd/C has been collected and reused by filtration, washing and drying after the reaction. The H₂ evolution has been re-initiated by adding the re-obtained Pd/C into another fresh solution of B₂pin₂ and H₂O. The result exhibited that Pd/C catalyst has been reused 5 times with a slightly decrease in the catalytic activity.



Figure 5. Hydrogen evolution from B₂pin₂ with H₂O and D₂O.



Figure 6. The $B_{2}\text{pin}_{2}$ hydrolysis in the presence of 0.4 % Pd/C during the reusability test.



For further studying H₂ evolution upon the hydrolysis of B_2pin_2 catalyzed by Pd/C, the tandem reaction for the hydrogenation of 1,1-diphenylethylene and norbornene with H_{2} , in situ generated from B₂pin₂ hydrolysis, has been investigated in a sealed two-chamber system at 30 °C for 12 h (Figure S1), The result exhibits that all the hydrogenations afford 99% yield of the desired products, verifying the evolution of H₂ (Figure S2 and Figure S3). Moreover, the reaction product of (Bpin)₂O was also confirmed by NMR spectrum (Figure S4) and mass spectrum (Figure S5). While the D₂ was produced from the hydrolysis of B₂pin₂ with D₂O. This D₂ has been used for the in situ hydrogenations of 1,1-diphenylethylene and norbornene, respectively, catalyzed by Pd/C in the right side (Figure 7). For the hydrogenation of 1,1-diphenylethylene (1a) with D_2 , the benzylic position is 81% deuteriated whereas methyl group is







Figure 8. Proposed mechanism for the hydrolysis of B₂Pin₂ reaction

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50% deuteriated (Eq. 2 and Figure S6). The uneven and excessive distribution is probably attributed to the facile migration of H or D atoms between the homobenzylic and benzylic positions.^[33,34] For the hydrogenation of norbornene, the desired product 4b is provided in 99% yield (Eq. 3 and Figure S7), exactly verifying that both two D atoms of D_2 gas are provided from D₂O. This is contrary to other boron compounds hydrolysis (including NH₃BH₃, NaBH₄), which generates H₂ with only one H atom provided by water and the other one by boron compounds.[35]

A mechanistic proposal of Pd/C catalyzed B₂pin₂ hydrolysis based on our experimental results follows (Figure 8): originally, intermediate **A** has been formed by oxidative addition of B₂pin₂ and Pd/C. Then intermediate B is obtained from A after the attack of water molecules. Subsequently, B further isomerized into intermediate C smoothly. Next, the generation of a dihydride Pd(H)₂ species from C, via releasing a molecule of $(Bpin)_2O$, leads to the formation of H_2 .^[36]

Conclusion

In summary, a novel and efficient Pd/C-catalyzed hydrogen production from the hydrolysis of B₂pin₂ has been developed for the first time. Typically, B₂pin₂ is often applied as a current borylation source, and it has rarely been used for reduction reactions. Among them, Pd/C is a very cheap and commercial source of palladium, it shows efficient catalytic activity in the H₂ evolution even without ligands. We found Pd/C, as a heterogeneous catalyst, has been successfully recycled 5 times without any activity loss for H₂ evolution by simple filtration. Moreover, kinetic isotope effects (KIEs) and tandem reaction have confirmed both two H atoms of H₂ gas are provided from H₂O. This is contrary to other boron compounds hydrolysis (including $NH_{3}BH_{3}$, $NaBH_{4}$), which generates H_{2} with only one H atom provided by water and the other one by boron compounds. Note that the hydrolysis of B_2pin_2 in D_2O also provides an easy and useful synthesis of D₂. In addition, this system has enormous potential to be tapped in large-scale industrial production and utilization.

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Conflict of Interest

The authors declare no conflict of interest.



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- [1] X. L. Qiao, L. B. Niu, H. L. Zhang, X. Wen, Y. Y. Cao, G. Y. Bai, *Appl. Catal. B* 2017, 218, 721–730.
- [2] Z. K. Peng, H. Y. Wang, L. L. Zhou, Y. B. Wang, J. Gao, G. J. Liu, S. A. T. Redfern, X. L. Feng, S. Y. Lu, B. J. Li, Z. Y. Liu, *J. Mater. Chem. A* **2019**, *7*, 6676–6685.
- [3] H. Y. Wang, C. Y. Gao, R. Li, Z. K. Peng, J. H. Yang, J. Gao, Y. P. Yang, S. H. Li, B. J. Li, Z. Y. Liu, ACS Sustainable Chem. Eng. 2019, 7, 18744–18752.
- [4] X. Guo, M. G. Li, Y. Q. Liu, Y. R. Huang, S. Geng, W. W. Yang, Y. S. Yu, J. Colloid Interface Sci. 2020, 563, 405–413.
- [5] P. L. Zhang, X. Qiang, Acc. Chem. Res. 2017, 50, 1449–1458.
- [6] Q. Yao, Z. H. Lu, W. Huang, X. Chen, J. Zhu, J. Mater. Chem. A 2016, 4, 8579–8583.
- [7] a) L. Schlapbach, A. Zuttel, *Nature* 2001, *414*, 353–358; b) W. Zhou, D.-D.
 Huang, Y.-P. Wu, J. Zhao, T. Wu, J. Zhang, D.-S. Li, C. Sun, P. Feng, X. Bu, *Angew. Chem. Int. Ed.* 2019, *58*, 4227–4231.
- [8] P. Zhao, N. Cao, J. Su, W. Luo, G. Cheng, ACS Sustainable Chem. Eng. 2015, 3, 1086–1093.
- [9] R. V. Helmolt, U. Eberle, J. Power Sources 2007, 165, 833-843.
- [10] F. Seven, N. Sahiner, Int. J. Hydrogen Energy 2014, 39, 15455-15463.
- [11] U. Demirci, P. Miele, Phys. Chem. Chem. Phys. 2014, 16, 6872-6885.
- [12] Q. L. Zhu, Q. Xu, Energy Environ. Sci. 2015, 8, 478–512.
- [13] C. Wang, J. Tuninetti, Z. Wang, C. Zhang, R. Ciganda, L. Salmon, S. Moya, J. Ruiz, D. Astruc, J. Am. Chem. Soc., 2017, 139, 11610–11615.
- [14] F. Fu, C. L. Wang, Q. Wang, A. M. Martinez-Villacorta, A. Escobar, H. B. Chong, X. Wang, S. Moya, L. Salmon, E. Fouquet, J. Ruiz, D. Astruc, *J. Am. Chem. Soc.*, **2018**, *140*, 10034–10042.
- [15] Q. Wang, F. Y. Fu, S. Yang, M. M. Moro, M. D. L. A. Ramirez, S. Moya, L. Salmon, J. Ruiz, D. Astruc, ACS Catal. 2019, 9, 1110–1119.
- [16] Q. Wang, F. Y. Fu, A. Escobar, S. Moya, J. Ruiz, D. Astruc, ChemCatChem 2018, 10, 2673–2680.
- [17] C. Luo, F. Y. Fu, X. J. Yang, J. Y. Wei, C. L. Wang, J. Zhu, D. S. Huang, D. Astruc, P. X. Zhao, *ChemCatChem* 2019, *11*, 1643–1649.
- [18] W. H. Guo, H. Y. Zhao, Z. J. Luo, S. Zhang, X. G. Zhang, ACS Catal. 2019, 9, 38–43.
- [19] M. Shimizu, T. Fujimoto, H. Minezaki, T. Hata, T. Hiyama, J. Am. Chem. Soc. 2001, 123, 6947–6948.
- [20] X. Liu, M. Shimizu, T. Hiyama, Angew. Chem. Int. Ed. 2004, 43, 879–882; Angew. Chem. 2004, 116, 897–900.
- [21] O. A. Argintaru, D. Ryu, I. Aron, G. A. Molander, Angew. Chem. Int. Ed. 2013, 52, 13656–13660; Angew. Chem. 2013, 125, 13901–13905.
- [22] D. H. Tan, E. Lin, W. W. Ji, Y. F. Zeng, W. X. Fan, Q. Li, H. Gao, H. Wang, Adv. Synth. Catal. 2018, 360, 1032–1037.
- [23] a) S. P. Cummings, T.-N. Le, G. E. Fernandez, L. G. Quiambao, B. J. Stokes, J. Am. Chem. Soc. 2016, 138, 19, 6107–6110; b) K. A. Korvinson, H. K. Akula, C. T. Malinchak, D. Sebastian, W. Wei, T. A. Khandaker, M. R.

Andrzejewska, B. Zajc, M. K. Lakshman, *Adv. Synth. Catal.* 2020, *362*, 166–176.

- [24] Y. T. Xia, X. T. Sun, L. Zhang, K. Luo, L. Wu, Chem. Eur. J. 2016, 22, 17151–17155.
- [25] M. Flinker, H. Yin, R. W. Juhl, E. Z. Eikeland, J. Overgaard, D. U. Nielsen, T. Skrydstrup, Angew. Chem. Int. Ed. 2017, 56, 15910–15915; Angew. Chem. 2017, 129, 16126–16131.
- [26] S. Liu, Y. Zhou, Y. Sui, H. Liu, H. Zhou, Org. Chem. Front., 2017, 4, 2175– 2178.
- [27] Q. Xuan, Q. Song, Org. Lett. 2016, 18, 4250-4253.
- [28] D. P. Ojha, K. Gadde, K. R. Prabhu, Org. Lett. 2016, 18, 5062–5065.
- [29] S. Rao, K. R. Prabhu, Chem. Eur. J. 2018, 24, 13954–13962.
- [30] H. Y. Bao, B. W. Zhou, H. W. Jin, Y. K. Liu, J. Org. Chem. 2019, 84, 3579– 3589.
- [31] a) W. F. Chen, J. L. Shen, Y. P. Huang, X. Liu, D. Astruc, ACS Sustainable Chem. Eng. 2020, 8, 7513–7522; b) J. Shen, W. Chen, G. Lv, Z. Yang, J. Yan, X. Liu, Z. Dai, Int. J. Hydrogen Energy. 2021, 46, 796–805; c) N. Zhang, G. Liu, Y. Sun, Y. Wang, J. Yan, X. Liu, Catal. Lett. 2021, https:// doi.org/10.1007/s10562-020-03501–8.
- [32] X. Liu, D. Astruc, Adv. Synth. Catal. 2018, 360, 3426–3459.
- [33] Z. Li, T. He, L. Liu, W. Chen, M. Zhang, G. Wu, P. Chen, Chem. Sci. 2017, 8, 781–788.
- [34] C. Yu, J. Fu, M. Muzzio, T. Shen, D. Su, J. Zhu, S. Sun, Chem. Mater. 2017, 29, 1413–1418.
- [35] a) C. W. Hamilton, R. T. Baker, A. Staubitz, I. Manners, Chem. Soc. Rev. 2009, 38, 279–293; b) Q. L. Zhu, Q. Xu, Energy Environ. Sci. 2015, 8, 478–512; c) W. W. Zhan, Q. L. Zhu, Q. Xu, ACS Catal. 2016, 6, 6892–6905; d) B. J. Zhu, R. Q. Zou, Q. Xu, Adv. Energy Mater. 2018, 8, 1801193; e) Y. Liu, Z. Y. Zhang, Y. R. Fang, B. K. Liu, J. D. Huang, F. J. Miao, Y. A. Bao, B. Dong, Appl. Catal. B 2019, 252, 164–173; f) Q. Sun, N. Wang, T. Zhang, R. Bai, A. Mayoral, P. Zhang, Q. Zhang, O. Terasaki, J. Yu, Angew. Chem. Int. Ed. 2019, 58, 18570–18576; g) F. P. Kinik, T. N. Nguyen, E. Oveisi, B. Valizadeh, F. M. Ebrahim, A. Gadysiak, M. Mensi, K. C. Stylianou, J. Mater. Chem. A. 2019, 7, 23830–23837; h) Q. Sun, N. Wang, R. Bai, Y. Hui, T. Zhang, D. A. Do, P. Zhang, L. Song, J. Yu, Adv. Sci. 2019, 6, 1802350; j) D. S. Lu, J. H. Li, C. H. Lin, J. Y. Liao, Y. F. Feng, Z. T. Ding, Z. W. Li, Q. B. Liu, H. Li, Small 2019, 15, 1805460; j) Y. Huang, K. Zheng, X. Liu, X. Meng, D. Astruc, Inorg. Chem. Front. 2020, 7, 939–945; k) Q. Yao, Y. Ding, Z.-H. Lu, Inorg. Chem. Front. 2020, 7, 3837–3874.
- [36] a) D. P. Ojha, K. Gadde, K. R. Prabhu, Org. Lett. 2016, 18, 5062–5065;
 b) V. J. Olsson, S. Sebelius, N. Selander, K. J. Szabo, J. Am. Chem. Soc. 2006, 128, 4588–4589.

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The new H₂ evolution upon B₂pin₂ hydrolysis is efficiently catalyzed by Pd/ C. The kinetic isotope effects and tandem reaction have verified both two H atoms of H₂ gas are provided from H₂O. Note that the hydrolysis of B_2pin_2 in D_2O also provides an easy and useful synthesis of D_2 . In addition, this system has enormous potential to be tapped in large-scale industrial production and utilization. N. Li, J. Shen, Prof. Dr. X. Liu*

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