

Pd/C and Pd-B/C catalysts with a Pd loading of 5 wt% were synthesized through wet chemical reduction of NaBH_4 and dimethylamine borane (DMAB), respectively (see Supporting Information for details). TEM images for these as-prepared catalysts are shown in Figure 1. ICP-AES results show that ca. 6 at.% boron is incorporated into Pd-B/C, while the boron content in Pd/C- NaBH_4 is less than 3 at.%.

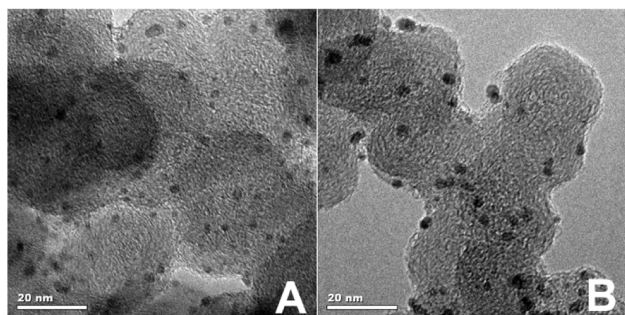


Figure 1. TEM images for 5 wt% (A) Pd/C and (B) Pd-B/C catalysts. The scale bars are 20 nm.

Figure 2 shows the volumes of gas generated from 10 mL solution of 1.1 M FA + 0.8 M SF (pH 3.5, around the pK_a of

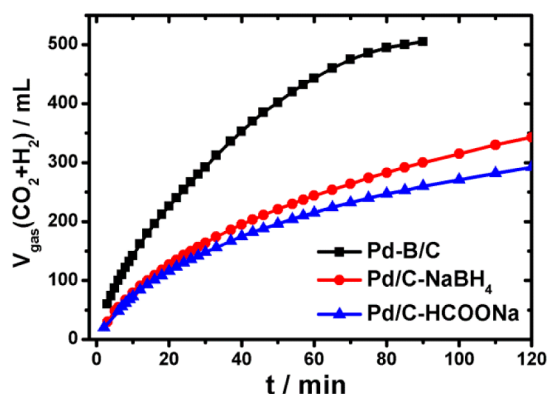


Figure 2. Time-course of reforming gas generation from 10 mL solution of 1.1 M FA + 0.8 M SF in the presence of 100 mg of Pd-based/C (5 wt% Pd) catalysts at 30 °C under ambient atmosphere.

FA) as a function of time with different Pd-based/C catalysts. To exclude any boron doping, HCOONa was used as the reducing agent instead of the commonly used NaBH_4 to synthesize Pd/C- HCOONa .¹⁵ Only a slightly higher gas production rate was observed on Pd/C- NaBH_4 than on Pd/C- HCOONa , suggesting a poor B-doping, if any, from borohydride. In contrast, the gas production rate is nearly doubled on Pd-B/C as compared to the other two catalysts at a given mass of Pd. After calibration of the sizes of nanocatalysts (i.e., ca. 4.1 nm for Pd-B/C and ca. 2.2 nm for Pd/C- NaBH_4), the TOF over the initial 15 min is calculated to be 1184 h^{-1} on Pd-B/C, nearly 4 times that on Pd/C- NaBH_4 (304 h^{-1}), suggesting a much higher activity from significant B-doping. Furthermore, compared to the TOF values reported so far for various Pd-based catalysts in FA-SF solutions, i.e., Pd/MSC-30 (750 h^{-1} at 298 K),³⁰ Pd- NH_2 /MIL-125 (214 h^{-1} at 305 K),³¹ Pd-Au-Dy/C (470 h^{-1} at 365 K),¹⁸ and Pd₃Ag₁/rGO (526 h^{-1} at 298 K),³² the present Pd-B/C catalyst show superior catalytic activity. As illustrated in our previous work on FA electro-oxidation, B atoms may be incorporated into Pd-Pd

inter-lattice spaces, leading to a slight expansion of Pd lattice, and serving as electron donors to optimize the electronic structure of Pd atoms for FA dehydrogenation.^{33,34} In XPS spectra (Figure S1), the $\text{Pd}^0 3d_{5/2}$ core-level binding energy for Pd-B/C is slightly upshifted with respect to the reference value for Pd, while that for Pd/C- NaBH_4 is virtually unshifted, indicating an effective electron transfer from B to Pd in the former (for more explanations on electron transfer direction, see Supporting Information).^{34,35} More catalytic evaluations on as-prepared Pd-B/C, Pd/C, and Pd₃Au/C¹² (at a constant Pd loading of 5 wt%) were also carried out at inclement condition, i.e., with 9.9 M FA + 3.3 M SF at 92 °C, as shown in Figure S2. It turns out that Pd-B/C yields the largest volume of the reforming gas within 150 min, and a rate of ca. $186 \text{ mL}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$ Pd after 2 h, superior to Pd₃Au/C but at a lower cost. The catalytic performance of Pd-B/C may be further improved through structural optimization of the carbon support, according to previous investigations on Pd/C.^{30,31}

GC measurement with a thermal conductivity detector (TCD) was performed to analyze the composition of the above reforming gas (Figure 3). The volumetric ratio of H_2 to CO_2 is

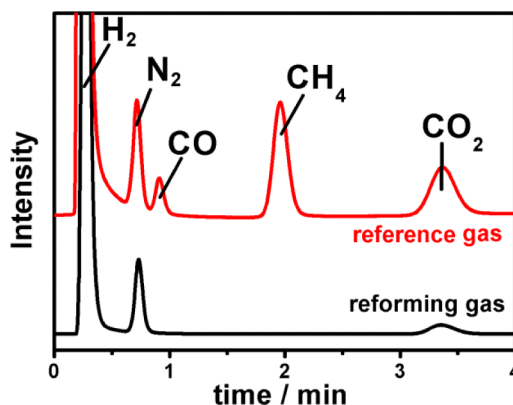


Figure 3. Gas chromatograms of the reforming gas and a reference gas recorded on a GC-TCD.

around 0.9:1 in the above open system (a slightly higher volume of CO_2 may come from the ambient air), arguing against the speculation of a significant contribution from the formate hydrolysis to hydrogen output.¹⁵ Furthermore, no gaseous CO signal was detected in all cases by GC recorded with a methanator and a flame ionization detector (see Figure S3), suggesting that its presence (if any) is lower than the detection limit of 1 ppm. The absence of detectable CO in the generated gas can be associated with a low operation temperature. Otherwise, at elevated temperatures, CO gas would be produced through water-gas shift reaction (Scheme 1).

To better understand the roles of FA and SF in the mixed solution, a control experiment of time-course of Pd-catalyzed gas production from 1.1 M FA, 1.1 M FA + 0.8 M SF, or 1.9 M FA was carried out over Pd/C- NaBH_4 at 30 °C. It is clearly seen from Figure 4A that the presence of formate ions in the solution significantly accelerates the hydrogen production rate, as in the case of homogeneous catalysis,^{24,25} whereas the initial concentration of FA has far less influence. Nevertheless, gas production from 0.8 M SF alone was too little to be measured, suggesting a negligible contribution from direct formate hydrolysis ($\text{HCOO}^- + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{HCO}_3^-$).³⁰ Adsorbed formate was suggested either to induce a favorable adsorption

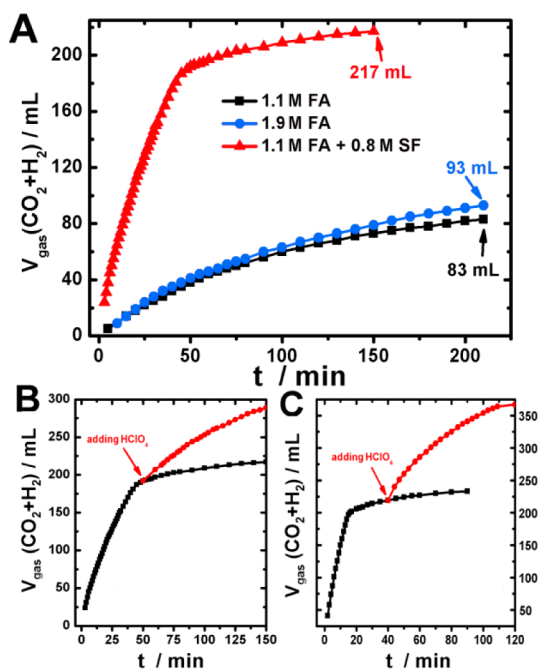


Figure 4. (A) Time-course of reforming gas generation from 5 mL of different solutions in the presence of 100 mg of Pd/C-NaBH₄ catalyst at 30 °C under ambient atmosphere. (B,C) Gas generation over 100 mg of Pd/C-NaBH₄ (B) or Pd-B/C (C) catalyst in 5 mL of 1.1 M FA + 0.8 M SF with (red) or without (black) addition of 5.5 mmol of HClO₄.

orientation of FA (H-down) on the catalyst to promote FA dehydrogenation^{36,37} or to act as a reactive intermediate for FA dehydrogenation.^{38,39} Also noted is the presence of an inflection point for the 5-mL FA-SF solution with a faster gas production (or a faster consumption of FA) before this point (ca. 81% FA was consumed at $t = 50$ min). To further understand this, aliquots of HClO₄ solution were added to supply hydrogen (or FA). A surge of hydrogen gas production can be seen from Figure 4B. These results suggest that formate ions promote FA dehydrogenation and the inflection point arises when FA in the solution is exhausted. Similar catalytic behavior was observed on Pd-B/C, albeit the inflection point appeared at a much shorter time (ca. 15 min, Figure 4C), reinforcing the superior catalytic activity of Pd-B/C. It should be pointed out that this is the first report regarding a metallo-doped nanocatalyst for hydrogen generation from FA decomposition.

In order to provide insight into the improved catalytic performance of the Pd-B/C, time-evolved ATR-IR measurements on Pd/C-NaBH₄ and Pd-B/C were performed in the FA-SF solution (see Scheme S1 and Figure S4). The strong bands at 1584, 1384, and 1351 cm⁻¹ in Figure 5 can be assigned to the solution formate, and a bulk FA peak appears at 1720 cm⁻¹. Augmentation of the bulk signals within the initial 30 s arises from the diffusion of the FA-SF solution to the catalyst surface following its injection. The CO₂ produced (together with H₂ production in the FA dehydrogenation) and dissolved in the solution can be identified from the weak band at 2345 cm⁻¹. A band at 1430 cm⁻¹ due to HCO₃⁻/CO₃²⁻ can also be clearly observed after 600 s. For comparison, the ATR-IR spectra of aqueous FA, SF, and their mixture on a bare Si prism, as well as the spectra of CO_{ad} on Pd-B/C and Pd/C-NaBH₄, are included in Figures S5 and S6.

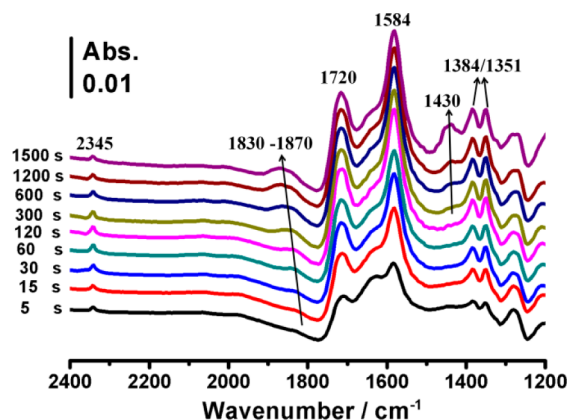


Figure 5. Selected ATR-IR spectra on Pd-B/C catalyst recorded after injection of a premixed 1.1 M FA + 0.8 M SF solution to the spectral cell. The reference spectrum was recorded in air before the injection. The band around 1280 cm⁻¹ may arise from $\nu(\text{C-O})$ of carbon black surfaces.

More importantly, Figure 5 shows the distinct feature of bridge-bonded CO (CO_B) on Pd nanoparticle surfaces, as can be seen from the gradually increased shoulder peaks from ca. 1830 to 1870 cm⁻¹,⁴⁰ despite the fact that no CO gas was detected by GC. According to our previous study,^{28,29} the slow accumulation of low-coverage CO_{ad} at Pd surfaces arises mainly from the reduction of the dehydrogenation product CO₂ rather than direct dehydration of FA. To further address the role of CO_{ad}, a control experiment was carried out by adding CO-saturated FA-SF solution to 100 mg of Pd/C-NaBH₄ catalyst. As a result, less than 1 mL of reforming gas was generated in 3 h, demonstrating fatal poisoning of catalytic sites by adsorbed CO.

Along this line, Figure 6 illustrates the time-evolved frequency of the $\nu(\text{CO}_B)$ band on Pd/C-NaBH₄ and Pd-B/C

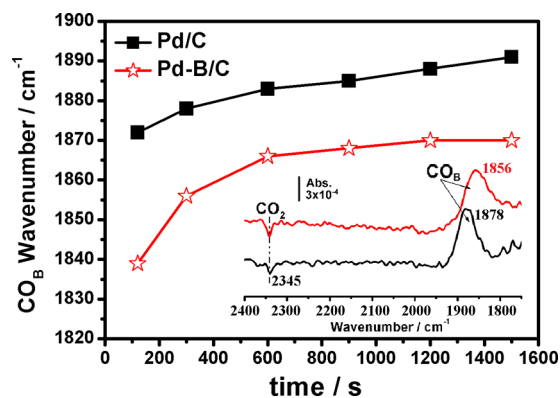


Figure 6. Time-course of changing C–O stretching frequency of bridge-bonded CO (CO_B) on Pd/C and Pd-B/C catalysts. The inset spectra were recorded 300 s after FA-SF injection, using the single-beam spectrum acquired at 60 s as the reference spectrum.

taken from a series of ATR-IR spectra recorded in 1.1 M FA + 0.8 M SF, and the inset shows the ATR-IR spectra at 300 s after spectral subtraction of the bulk FA signals acquired at 60 s. A lower frequency of the $\nu(\text{CO}_B)$ band on Pd-B/C throughout ATR-IR measurements was observed, suggesting a lower CO_{ad} coverage or an enhanced anti-poisoning ability, given that the $\nu(\text{CO}_{ad})$ band center frequency increases with CO coverage on metal surfaces. In other words, slower CO_{ad} accumulation may

at least partly account for enhanced Pd-catalyzed hydrogen production from a FA-SF solution with Pd-B/C. Furthermore, the Pd-B nanoparticles have a slightly expanded Pd lattice, which is similar to the effective Pd/Au(Ag) nanoalloy and Ag@Pd nanoparticles used in the literature.^{17,21,23} This structural change may increase the adsorption of formate ions, which in turn may induce an H-down orientation of FA molecules approaching Pd surfaces,^{36,37} enabling FA dehydrogenation to occur at a lower activation energy. The above correlations could be used to guide the rational design of new Pd-based catalysts. Last but not least, this work demonstrates that efficient Pd-based catalysts for hydrogen production can now be achieved without the inclusion of another noble metal. Future work will aim to understand the higher activity of Pd-B catalyst via DFT calculations and to optimize the size of Pd-B nanoparticles and the structure of the support.

In summary, we present an initial report on metalloid-doped Pd nanocatalysts for efficient H₂ production from aqueous FA-SF at ambient conditions. The TOF reaches 1184 h⁻¹ at 30 °C on Pd-B/C and is ca. 3 times higher than that on Pd/C. Furthermore, CO_{ad} accumulation on Pd surfaces during hydrogen generation is detected by high-sensitivity ATR-IR measurement, even though CO content in the gas is below 1 ppm, if any. Lower coverage of CO on Pd-B/C catalyst as compared to Pd/C correlates with the enhanced hydrogen production on the former. The effective metalloid doping coupled with high sensitivity ATR-IR measurements offers a promising approach to designing new catalysts for efficient dehydrogenation of formic acid.

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental details, additional material characterization, and evaluation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

wbcai@fudan.edu.cn

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work is supported by NSFC (Nos. 21073045 and 21273046), SMCST (Nos. 11JC140200 and 08DZ2270500). We appreciate Profs. Minghua Qiao and Weilin Dai, and Dr. Chao Wen for GC measurements.

■ REFERENCES

- (1) Boddien, A.; Loges, B.; Gärtner, F.; Torborg, C.; Fumino, K.; Junge, H.; Ludwig, R.; Beller, M. *J. Am. Chem. Soc.* **2010**, *132*, 8924.
- (2) Yadav, M.; Xu, Q. *Energy Environ. Sci.* **2012**, *5*, 9698.
- (3) Whipple, D. T.; Kenis, P. J. A. *J. Phys. Chem. Lett.* **2010**, *1*, 3451.
- (4) Grasemann, M.; Laurenczy, G. *Energy Environ. Sci.* **2012**, *5*, 8171.
- (5) Capon, A.; Parsons, R. *J. Electroanal. Chem.* **1973**, *45*, 205.
- (6) Gu, X.; Lu, Z.-H.; Jiang, H.-L.; Akita, T.; Xu, Q. *J. Am. Chem. Soc.* **2011**, *133*, 11822.
- (7) Solymosi, F.; Koos, A.; Liliom, N.; Ugrai, I. *J. Catal.* **2011**, *279*, 213.
- (8) Chen, A.; Holt-Hindle, P. *Chem. Rev.* **2010**, *110*, 3767.
- (9) Cuesta, A.; Cabello, G.; Osawa, M.; Gutierrez, C. *ACS Catal.* **2012**, *2*, 728.
- (10) Ojeda, M.; Iglesia, E. *Angew. Chem., Int. Ed.* **2009**, *48*, 4800.

- (11) Bi, Q. Y.; Du, X. L.; Liu, Y. M.; Cao, Y.; He, H. Y.; Fan, K. N. *J. Am. Chem. Soc.* **2012**, *134*, 8926.
- (12) Zhou, X. C.; Huang, Y. J.; Xing, W.; Liu, C. P.; Liao, J. H.; Lu, T. H. *Chem. Commun.* **2008**, 3540.
- (13) Bulushev, D. A.; Jia, L. J.; Beloshapkin, S.; Ross, J. R. H. *Chem. Commun.* **2012**, *48*, 4184.
- (14) Jones, S.; Qu, J.; Tedsree, K.; Gong, X. Q.; Tsang, S. C. E. *Angew. Chem., Int. Ed.* **2012**, *51*, 11275.
- (15) Wang, Z. L.; Yan, J. M.; Wang, H. L.; Ping, Y.; Jiang, Q. *Sci. Rep.* **2012**, *2*, 598.
- (16) Mori, K.; Dojo, M.; Yamashita, H. *ACS Catal.* **2013**, 1114.
- (17) Huang, Y. J.; Zhou, X. C.; Yin, M.; Liu, C. P.; Xing, W. *Chem. Mater.* **2010**, *22*, 5122.
- (18) Zhou, X. C.; Huang, Y. J.; Liu, C. P.; Liao, J. H.; Lu, T. H.; Xing, W. *ChemSuschem* **2010**, *3*, 1379.
- (19) Gu, X. J.; Lu, Z. H.; Jiang, H. L.; Akita, T.; Xu, Q. *J. Am. Chem. Soc.* **2011**, *133*, 11822.
- (20) Wang, Z. L.; Yan, J. M.; Ping, Y.; Wang, H. L.; Zheng, W. T.; Jiang, Q. *Angew. Chem., Int. Ed.* **2013**, *52*, 4406.
- (21) Zhang, S.; Metin, O.; Su, D.; Sun, S. H. *Angew. Chem., Int. Ed.* **2013**, *52*, 3681.
- (22) Metin, O.; Sun, X. L.; Sun, S. H. *Nanoscale* **2013**, *5*, 910.
- (23) Tedsree, K.; Li, T.; Jones, S.; Chan, C. W. A.; Yu, K. M. K.; Bagot, P. A. J.; Marquis, E. A.; Smith, G. D. W.; Tsang, S. C. E. *Nat. Nanotechnol.* **2011**, *6*, 302.
- (24) Fellay, C.; Yan, N.; Dyson, P. J.; Laurenczy, G. *Chem.—Eur. J.* **2009**, *15*, 3752.
- (25) Fellay, C.; Dyson, P. J.; Laurenczy, G. *Angew. Chem., Int. Ed.* **2008**, *47*, 3966.
- (26) Ting, S. W.; Cheng, S. A.; Tsang, K. Y.; van der Laak, N.; Chan, K. Y. *Chem. Commun.* **2009**, 7333.
- (27) Kakuta, S.; Abe, T. *ACS Appl. Mater. Interfaces* **2009**, *1*, 2707.
- (28) Wang, J. Y.; Zhang, H. X.; Jiang, K.; Cai, W. B. *J. Am. Chem. Soc.* **2011**, *133*, 14876.
- (29) Zhang, H. X.; Wang, S. H.; Jiang, K.; Andre, T.; Cai, W. B. *J. Power Sources* **2012**, *199*, 165.
- (30) Zhu, Q.-L.; Tsumori, N.; Xu, Q. *Chem. Sci.* **2014**, *5*, 195.
- (31) Martis, M.; Mori, K.; Fujiwara, K.; Ahn, W.-S.; Yamashita, H. *J. Phys. Chem. C* **2013**, *117*, 22805.
- (32) Ping, Y.; Yan, J.-M.; Wang, Z.-L.; Wang, H.-L.; Jiang, Q. *J. Mater. Chem. A* **2013**, *1*, 12188.
- (33) Wang, J. Y.; Kang, Y. Y.; Yang, H.; Cai, W. B. *J. Phys. Chem. C* **2009**, *113*, 8366.
- (34) Carencio, S.; Portehault, D.; Boissière, C.; Mézailles, N.; Sanchez, C. *Chem. Rev.* **2013**, *113*, 7981.
- (35) Wakisaka, M.; Mitsui, S.; Hirose, Y.; Kawashima, K.; Uchida, H.; Watanabe, M. *J. Phys. Chem. B* **2006**, *110*, 23489.
- (36) Wang, H. F.; Liu, Z. P. *J. Phys. Chem. C* **2009**, *113*, 17502.
- (37) Peng, B.; Wang, H. F.; Liu, Z. P.; Cai, W. B. *J. Phys. Chem. C* **2010**, *114*, 3102.
- (38) Gao, W.; Keith, J. A.; Anton, J.; Jacob, T. *J. Am. Chem. Soc.* **2010**, *132*, 18377.
- (39) Joo, J.; Uchida, T.; Cuesta, A.; Koper, M. T. M.; Osawa, M. *J. Am. Chem. Soc.* **2013**, *135*, 9991.
- (40) Mojet, B. L.; Ebbesen, S. D.; Lefferts, L. *Chem. Soc. Rev.* **2010**, *39*, 4643.