Electronic Supplementary Information for

Crystal phase-selective synthesis of intermetallic palladium borides and phase-regulated (electro)catalytic properties

Zhenyu Li, a, b, ‡ Linmin Zhao, c, ‡ Hui Chen, a Xiao Liang, a Xuan Ai, a Zhoubing Xie, a
Xiaotian Li, b Feng Yang, d Hongyang Liu, c * and Xiaoxin Zou, a,*

a State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, P. R. China.
b College of Materials Science and Engineering, Jilin University, Changchun 130022, P. R. China.
c Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China.
d Department of Chemistry, Southern University of Science and Technology, Shenzhen, 518055, China

‡ Z.Li and L.Zhacontributed equally to this work.

* E-mail: xxzou@jlu.edu.cn, liuhy@imr.ac.cn
1 Theoretical Section

1.1 Computation Details

The DFT calculations were conducted in the frame of Vienna ab initio simulation package (VASP). The Perdew-Burke-Ernzerhof (PBE) exchange correlation functional was adopted with generalized gradient approximation (GGA). For all calculations, a k-point separation length of 0.04 Å\(^{-1}\) was used for the Brillouin zones, which were processed by the VASPKIT code. During all process calculations, the cutoff energy of plane-wave basis was 400 eV with 10\(^{-4}\) eV of energy convergence and 0.02 eV Å\(^{-1}\) of force convergence. Especially for slabs, DFT-D2 method was used to correct the van der Waals interaction with symmetrization and taking dipolar correction into account. The LOBSTER was used to perform crystal orbital Hamiltonian population (COHP).

For the slab models of HER calculations, we constructed Pd(111), Pd\(_6\)B(001), Pd\(_5\)B\(_2\)(010) and Pd\(_2\)B(010), which are closed-packed surfaces. Six atomic layers were constructed in Pd(111) and four metal atomic layers were constructed in Pd\(_6\)B(001), Pd\(_5\)B\(_2\)(010) and Pd\(_2\)B(010) with metal terminations. For all slabs, the vacuum layer was 15 Å to avoid interlayer interactions. During structural optimization of slabs, the lower half of atomic layers was kept frozen and the upper half was fully relaxed.

1.2 Computation of Gibbs free-energy (\(\Delta G_{H^*}\)) for hydrogen evolution reaction

To calculate the Gibbs free-energy (\(\Delta G_{H^*}\)) of the hydrogen adsorption, we used the equation:

\[
\Delta G_{H^*} = \Delta E_{H^*} + \Delta ZPE - T\Delta S
\]  

The \(\Delta E_{H^*}\), \(\Delta S\) and \(\Delta ZPE\) were the adsorption energy, entropy change of \(H^*\) adsorption and zero-point energy, respectively. According to the ideas proposed by Nørskov et al.,\(^{10}\) the vibrational entropy of \(H^*\) was negligible. Therefore, we can obtain \(\Delta S\) and \(\Delta ZPE\) by equation:

\[
\Delta S = S(H^*) - \frac{1}{2} S(H_2) \approx -\frac{1}{2} S(H_2)
\]  

\[
\Delta ZPE = ZPE(H^*) - \frac{1}{2} ZPE(H_2)
\]

As a result, the value of \(T\Delta S\) is \(-0.205\) eV because \(TS(H_2)\) is equal to 0.41 eV for \(H_2\) at 298 K and 1 atm.

Without the consideration of \(H^*\) coverage, we obtained the adsorption energy of hydrogen by equation:

\[
\Delta E_{H^*} = E(\text{surface } + H^*) - E(\text{surface}) - \frac{1}{2} E(H_2)
\]  

where \(E(\text{surface } + H), E(H_2)\) and \(E(\text{surface})\) are the energies of the surface adsorbed with one H atom, hydrogen molecule and the clear surface, respectively.
1.3 Computation of $d$-band center

We attained $d$-band center by equation:\(^{11}\)

\[
\varepsilon_d = \frac{\int \limits_{-\infty}^{\infty} n_d(\varepsilon) \varepsilon d\varepsilon}{\int \limits_{-\infty}^{\infty} n_d(\varepsilon) d\varepsilon}
\]

where $\varepsilon$ is the energy referring to E-Fermi and $n_d(\varepsilon)$ is density of states projected onto $d$-states.

1.4 Computation of the energy barrier of the breakage of C-I bonds for iodobenzene on the Pd(111) and Pd$_2$B(010) surface

The adsorption of iodobenzene molecule on the surface of Pd(111) and Pd$_2$B(010) was the initial state, and the adsorption of isolated phenyl and iodine atom was the final state. The transition state of the reaction was calculated by the climbing image nudged elastic band (CI-NEB) method. Meanwhile, the transition state of reaction was acquired by vibrational frequency analysis.\(^{12}\) The optimized adsorption models of the initial, transition and final states on the Pd$_2$B(010)surface have been showed in the main text (Figure 3f). The activation energy ($E_a$) of reaction was calculated according to the below equation:

\[
E_a = E_{TS} - E_{ini}
\]

where $E_{TS}$ and $E_{ini}$ are the energies of transition state and initial state, respectively.

2 Experimental Section

2.1 Chemicals and Reagents

Sodium tetrachloropalladate (Na$_2$PdCl$_4$) was purchased from Aladdin Chemistry Co., Ltd. Magnesium diborides (MgB$_2$) was obtained from Alfa Aesar Chemicals Co., Ltd. Iodobenzene was purchased from Aladdin Chemistry Co., Ltd. Ethanol and sulfuric acid (H$_2$SO$_4$) were purchased from Beijing Chemical Factory. Palladium on graphitized carbon (20 wt% Pt/C) was bought from Sigma-Aldrich. Phenylboronic acid was supplied by Shanghai Macklin Biochemical Co., Ltd. K$_2$CO$_3$ was purchased from Sinopharm Chemical Reagent Co., Ltd. Highly purified water (>18 MΩ cm resistivity) was provided by a PALL PURELAB Plus system.

2.2 Materials Synthesis
2.2.1 Synthesis of Pd$_2$B particles. The Pd$_2$B was prepared by solid phase reaction with the molar ratio of 1:1 of Na$_2$PdCl$_4$ and MgB$_2$. The above Na$_2$PdCl$_4$ and MgB$_2$ were placed into a mortar, and then were ground to a uniform mixture. Subsequently, the mixture was sealed in a quartz tube with vacuum atmosphere of 0.9 Pa. After, the above sealed quartz tube was heated at 500 °C with a rate of 3 °C min$^{-1}$, and maintained for 2h in a muffle furnace. In order to remove the impurities of NaCl and MgCl$_2$, the acquired black powder from quartz tube was dispersed in a diluted H$_2$SO$_4$ solution (0.5 M), and held for 4h. Finally, the product of Pd$_2$B was obtained after washing three times with deionized water and ethanol, and dried with the temperature of 60 °C.

2.2.2 Synthesis of Pd$_5$B$_2$ particles. The Pd$_5$B$_2$ was prepared by solid phase reaction with the molar ratio of 1:0.8 of Na$_2$PdCl$_4$ and MgB$_2$. The above Na$_2$PdCl$_4$ and MgB$_2$ were placed into a mortar, and then were ground to a uniform mixture. Subsequently, the mixture was sealed in a quartz tube with vacuum atmosphere of 0.9 Pa. After, the above sealed quartz tube was heated at 500 °C with a rate of 3 °C min$^{-1}$, and maintained for 1h in a muffle furnace. In order to remove the impurities of NaCl and MgCl$_2$, the acquired black powder from quartz tube was dispersed in a diluted H$_2$SO$_4$ solution (0.5 M), and held for 4h. Finally, the product of Pd$_5$B$_2$ was obtained after washing three times with deionized water and ethanol, and dried with the temperature of 60 °C.

2.2.3 Synthesis of Pd$_6$B particles. The Pd$_6$B was prepared by solid phase reaction with the molar ratio of 1:0.8 of Na$_2$PdCl$_4$ and MgB$_2$. The above Na$_2$PdCl$_4$ and MgB$_2$ were placed into a mortar, and then were ground to a uniform mixture. Subsequently, the mixture was sealed in a quartz tube with vacuum atmosphere of 0.9 Pa. After, the above sealed quartz tube was heated at 500 °C with a rate of 3 °C min$^{-1}$, and maintained for 1h in a muffle furnace. In order to remove the impurities of NaCl and MgCl$_2$, the acquired black powder from quartz tube was dispersed in a diluted H$_2$SO$_4$ solution (0.5 M), and held for 4h. Finally, the product of Pd$_6$B was obtained after washing three times with deionized water and ethanol, and dried with the temperature of 60 °C.

2.2.4 Synthesis of Pd particles. The Pd was prepared by solid phase reaction with the molar ratio of 1:4 of Na$_2$PdCl$_4$ and Mg. The above Na$_2$PdCl$_4$ and Mg were placed into a mortar, and then were ground to a uniform mixture. Subsequently, the mixture was sealed in a quartz tube with vacuum atmosphere of 0.9 Pa. After, the above sealed quartz tube was heated at 450 °C with a rate of 3 °C min$^{-1}$, and maintained for 1h in a muffle furnace. In order to remove the impurities of MgCl$_2$ and Mg, the acquired black powder from quartz tube was dispersed in a diluted H$_2$SO$_4$ solution (0.5 M), and held for 4h. Finally, the product of Pd was obtained after washing three times with deionized water and ethanol, and dried with the temperature of 60 °C.
2.2.5 Synthesis of Ptparticles. The Pt was prepared by solid phase reaction with the molar ratio of 1:4 of PtCl$_4$ and Mg. The above PtCl$_4$ and Mg were placed into a mortar, and then were ground to a uniform mixture. Subsequently, the mixture was sealed in a quartz tube with vacuum atmosphere of 0.9 Pa. After, the above sealed quartz tube was heated at 500 °C with a rate of 3 °C min$^{-1}$, and maintain 4h in a muffle furnace. In order to remove the impurities of MgCl$_2$ and Mg, the acquired black powder from quartz tube was dispersed in a diluted H$_2$SO$_4$ solution (0.5 M), and held for 4h. Finally, the product of Pt was obtained after washing three times with deionized water and ethanol, and dried with the temperature of 60 °C.

2.3 Material Characterizations

The powder X-ray diffraction (XRD) patterns were obtained on X-ray diffractometer (Rigaku D/Max 2550) using Cu K$_\alpha$ radiation ($\lambda = 1.5418$ Å). The transmission electron microscope (TEM) images and high resolution TEM (HRTEM) images were performed on a Philips- FEI Tecnai G2STwin microscope operating at a field emission gun operating at 200 kV. The scanning electron microscope (SEM) images and Energy dispersive X-ray (EDX) spectroscopy were performed on a JEOL JSM 6700F electron microscope. The X-ray photoemission spectroscopy (XPS) spectra of samples were recorded on a Thermo Fisher Scientific ESCALAB 250Xi with photoelectron spectroscopy system of monochromatic Al K$_\alpha$ (1486.6 eV) X-ray source. The surface area of catalysts was calculated by the Brunauer-Emmett-Teller (BET) method by a Micromeritics ASAP 2020M system. H$_2$ temperature-programmed reduction characterizations (H$_2$-TPR) were conducted at a Micromeritics AutoChem 2920 II system.

2.4 Electrochemical Measurements

HER performance of Pd, Pd$_6$B, Pd$_5$B$_2$ and Pd$_2$B samples were measured by using electrochemical workstation (CHI 660E), and then record the electrocatalytic properties of all catalysts. The electrocatalytic performance of catalysts were operated in acidic medic with N$_2$-saturated diluted H$_2$SO$_4$ solution (0.5 M). The standard three-electrode system is consisted of a carbon rod as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode and glassy carbon electrode as working electrode. In order to enable the accuracy of catalytic performance for all catalysts, we used the Boettcher's method to correct the SCE.$^{13}$ For a typical preparation process of working electrode, we dropped a ink of Pd$_2$B catalyst on GCE (3 mm diameter). The catalyst ink was obtained by dispersing Pd$_2$B catalyst (8 mg) in isopropanol(400 µL) with conductive polymer binder (0.3% Nafion solution, 400 µL), and then ultrasonicated 30 min to form uniform suspension. After, the GCE was coated by using 4 µL of the above ink, lead to a catalyst loading about 0.562 mg cm$^{-2}$. Finally, the above electrode was dried in the air.
Linear sweep voltammetry (LSV) curve of catalysts was recorded, and then the scan rate was set to 1 mV s\(^{-1}\). In the above measured process of LSV, the iR-drop (ohmic compensation) was set to 85%. Based on the method of Jaramillo et al, we used the positive feedback to acquire the 85% iR-compensations. The potential (or overpotential) was corrected by using Nernst equation as well the equation:

\[
E_{\text{vs.RHE}} = E_{\text{vs.SCE}} + 0.263 \text{ eV} + 0.059pH
\]  

(7)

In order to evaluate their catalytic performance, we also prepare the working electrode with same catalyst loading for Pd, Pd\(_6\)B, Pd\(_5\)B\(_2\) and Pt, and then measure their catalysis performance under the same conditions as above.

2.4.1 Estimation of electrochemically active surface area (ECSA). The ECSA of all the catalysts were evaluated by geometric double layer capacitance (\(C_{\text{dl}}\)). The \(C_{\text{dl}}\) of catalysts were acquired by conducting cyclic voltammetry (CV) measurements. In typical experiment, the scan rates was set to 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 mV/s, and then the potential range was set to 0.4 - 0.5 V versus SCE. In order to enable the consistency of CV curve in the measurements, the sweep segments were set to 30. Subsequently, we fit the line relation by calculation the ration between the \(J_{\text{anodic}} - J_{\text{cathodic}}\) at 0.45 V versus SCE against the scan rate, and then acquire a slope. The above slope is equal to twice \(C_{\text{dl}}\). The twice of \(C_{\text{dl}}\) value is equal to the ECSA of the catalyst. The ECSA of catalyst was calculated by the equation:

\[
\text{ECSA} = \frac{C_{\text{dl}}}{C_s}
\]  

(8)

where \(C_s\) (the value is 0.04 mF/cm\(^2\)) represents the specific capacitance of catalyst. \(S\) represents the geometric area of glassy carbon electrode (\(S = 0.071 \text{ cm}^2\)).

2.4.2 Determination of Faradaic efficiency. The calculation of Faradic efficiency by using the equation:

\[
\text{Faradic efficiency} = \frac{\text{The actual amount of evolved hydrogen gas}}{\text{The theoretical amount of evolved hydrogen gas}}
\]  

(9)

Where the actual amount of evolved hydrogen gas was calculated by water drainage method in a home-made equipment.\(^{14}\) The theoretical amount of evolved hydrogen gas was calculated by using the Faraday law. When 1 equivalent of reaction happen, which means the passage of 96485.4 C charge was transferred for equation of Faraday law.

2.5 Catalytic performance measurement of Suzuki cross-coupling reaction.

2.5.1 Suzuki cross-coupling reaction. The reaction was carried out in a 5 mL glass reaction flask equipped with magnetic stirrer. In a typically reaction procedure,
iodobenzene (0.5 mmol), phenylboronic acid (0.8 mmol), K$_2$CO$_3$ (1.5 mmol), Pd catalysts (40mol% relative to iodobenzene) were added to 5 mL ethanol in reaction flask. Then the reactor was purged by N$_2$ for six times to remove residual air at 60 °C. The products were analyzed by gas chromatography(GC) and n-octane as the internal standard.

The TOF values were calculated by formula as follows:

$$\text{TOF} = \frac{n_0C}{tn_{\text{cat}}}$$

where $n_0$ represents the initial moles of iodobenzene, $C$ represents the conversion of reactant at reaction time, $n_{\text{cat}}$ represents the total moles of Pd species on the catalysts.

2.5.2 Stability test. Stability test of our catalysts followed same reaction conditions described above, expecting to use the recycled catalysts. In order to remove impurities after each reaction, the catalyst was separated by centrifugation and washed with water and ethanol for several times. Finally, the recycled catalysts were dried at 60 °C in vacuum for 4h, and then recorded its weight and reused in the next cycle.
Figure S1 SEM of (a) Pd, (b) Pd₆B, (c) Pd₅B₂ and (d) Pd₂B particles.

Table S1 The BET surface areas (m²/g) of Pd, Pd₆B, Pd₅B₂ and Pd₂B particles.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pd</th>
<th>Pd₆B</th>
<th>Pd₅B₂</th>
<th>Pd₂B</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET surface area (m²/g)</td>
<td>6.13</td>
<td>6.92</td>
<td>8.33</td>
<td>7.42</td>
</tr>
</tbody>
</table>
Figure S2 (a) Pd 3d XPS spectra of Pd₆B, Pd₅B₂, Pd₂B and metallic Pd samples. (b) B 1s XPS spectra of Pd₆B, Pd₅B₂, Pd₂B and B samples. The location of dotted frame in (b) is attributed to BOₓ Species.¹⁵-¹⁶

Figure S3 (a) H₂-TPR profiles and (b) H₂ consumption amount of Pd₂B, Pd₅B₂, Pd₆B and metallic Pd samples. The inset in (b) shows the inhibition effect of hydrogen uptake by interstitial boron atoms in Pd-B intermetallics. Blue, yellow, and gray spheres show Pd, B and H atoms, respectively.

Figure S4 LSV curves for HER over Pd₂B, and commercial Pt/C.
Figure S5 Electrocatalytic efficiency of Pd$_2$B toward the HER in 0.5 M H$_2$SO$_4$ solution at a current density of 10 mA cm$^{-2}$. The red line represents the theoretical amount of hydrogen based on the measured current density, and the gray dot represents the amount of hydrogen detected experimentally.

Figure S6 Tafel plots for HER over Pd, Pd$_6$B, Pd$_5$B$_2$, Pd$_2$B and Pt.

Figure S7 COHP of Pd-B bond for (a) Pd$_2$B, (b) Pd$_5$B$_2$ and (c) Pd$_6$B models.
Figure S8 Density of states of Pd, Pd₆B, Pd₅B₂ and Pd₂B.

Figure S9 The structural models of (a) Pd, (b) Pd₆B, (c) Pd₅B₂ and (d) Pd₂B. Blue and green spheres show Pd and B atoms, respectively.
We conducted a set of Arrhenius plots based on the initial reaction rate \( (r_0) \) values at different reaction temperatures, and then the \( E_a \) was calculated by plotting \( \ln r_0 \) as a function of \( 1/T \). The slope of the Arrhenius plot was used to calculate the apparent \( E_a \) of Pd, Pd\(_6\)B, Pd\(_5\)B\(_2\) and Pd\(_2\)B catalysts for the Suzuki coupling of iodobenzene and phenylboronic acid. As shown in Figure S10, the \( E_a \) reduction of Pd\(_2\)B is 37.5 kJ/mol, which is remarkably lower than those of Pd (85.4 kJ/mol), Pd\(_6\)B (67.9 kJ/mol) and Pd\(_5\)B\(_2\) (63.2 kJ/mol), respectively. This result suggests that the Suzuki coupling reaction is highly promoted over Pd\(_2\)B.

**Figure S10** Apparent \( E_a \)s for Suzuki coupling reaction over Pd, Pd\(_6\)B, Pd\(_5\)B\(_2\) and Pd\(_2\)B catalysts.

**Figure S11** Conversion profiles for Suzuki coupling reaction over Pd, Pd\(_2\)B and Pd/C catalysts.
The average distance of adjacent Pd-Pd and Pd-B atoms for three palladium-boron intermetallics.

We used the density functional theory calculation (DFT) to further study the boron concentration influence on the distance of adjacent Pd-Pd and Pd-B atoms for Pd-B intermetallics. As shown in Figure S12, with the increase of B content in Pd-B intermetallics lattice, the distance of Pd-Pd atoms is decreased, whereas distance of Pd-B is increased.
The electron location function (ELF) can also be calculated to further reveal the bonding of B-B and Pd-Pd of these three Pd-B intermetallics. As shown in Figure S13, B-B bond does not form because of the long B-B distance for three Pd-B intermetallics. The Pd–Pd distance increases with the increase of boron content in Pd host lattice, while the Pd–B distance decreases with the increase of boron content in Pd host lattice. Besides, despite the Pd-Pd distance and Pd-B distance is significantly variabled in three Pd-B intermetallics with the elevated B concentration, these Pd-B intermetallics still remain the metallic bond.
Figure S14 (a-b) The models of iodobenzene absorbed on the Pd and Pd$_2$B surface for the final state of the Suzuki coupling reaction. Blue, orange, pink, caramel and gray spheres show Pd, B, I, C and H atoms, respectively.

Considering that Pd atom is easily dissolved on the metallic Pd catalyst surface during reaction process, Pd-based catalysts generally suffer from low catalysis activity and stability. As shown in Figure 13a, the surface reconstruction occurs on the Pd model, which means the Pd atoms on Pd catalyst were easily dissolved during catalysis process. Unlike the surface reconstruction of Pd model, the Pd$_2$B model remains the pristine surface structure after the final state of Suzuki coupling reaction, leading to an enhancement on catalysis stability for Suzuki coupling reaction (Figure S14).

Figure S15 XRD pattern of Pd$_2$B after recycling test.

Figure S16 HRTEM image of Pd$_2$B after recycling test.
References