Energy & Environmental Science



PAPER



Cite this: Energy Environ. Sci., 2019, **12**, 3099

Received 14th May 2019, Accepted 16th August 2019

DOI: 10.1039/c9ee01564g

rsc.li/ees

Broader context

Metal boride better than Pt: HCP Pd₂B as a superactive hydrogen evolution reaction catalyst[†]

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In the search for a highly active bulk material for the hydrogen evolution reaction (HER) under acidic conditions, we developed a simple solvothermal approach to synthesize Pd_2B nanosheets supported on carbon, which achieves a low overpotential for the HER, 15.3 mV at 10 mA cm⁻², a small Tafel slope of 22.5 mV dec⁻¹ and a high exchange current density (j_0) of 2.84 mA cm⁻². The atomic structure evolution from Pd to Pd₂B catalyst during synthesis is analyzed in detail *via* experimental and theoretical calculations, which shows that the slow insertion of B is assisted by the layer-by-layer fcc-to-hcp phase transition. Theoretical calculations further revealed that both the subsurface B and the lattice expansion after the hcp lattice formation play a key role to boost the HER activity. Since the Pd₂B crystal is the global minimum in the Pd–B alloy, the success in the synthesis and demonstration of high HER activity paves the way towards further exploration of the catalytic performance for this stable metal boride material.

The hydrogen evolution reaction (HER, $2H^+ + 2e^- \rightarrow H_2$) in water splitting is regarded as a key chemical reaction towards a clean energy society. The harsh reaction conditions, *i.e.* low pH and low electrochemical potential, have limited its large-scale applications due to the high cost and poor long-term stability of the catalyst, commonly platinum (Pt) based materials. Modern research *via* quantum mechanics simulations indicates that the high activity of the Pt catalyst is attributed to the apex sites of the ultrasmall nanoparticles, which are intrinsically prone to aggregation. Our previous theoretical efforts thus focused on the search for stable crystalline materials with high HER activity on their close-packed surfaces, and palladium boride Pd₂B was identified as such a candidate. Here we report a simple solvothermal approach to obtain for the first time Pd₂B nanosheets on a large-scale, and show that this metal boride indeed has both a record high intrinsic activity (activity per surface site), ~ 2 times higher than that of commercial Pt/C, and a high stability under the reaction conditions. We demonstrate that the combination of theory and experiment represents a rational and cost-effective strategy to understand the physics in complex reaction processes and to design new catalysts for challenging systems.

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† Electronic supplementary information (ESI) available: Experimental methods and calculation details, SEM and TEM images, magnetic susceptibility, XPS pattern, CO stripping, XRD, exchange current densities, polarization curves and structures of further B diffusion without the fcc-to-hcp transition. See DOI: 10.1039/c9ee01564g

Introduction

The hydrogen evolution reaction (HER, $2H^+ + 2e^- \rightarrow H_2$) is a key component in water splitting for generating clean energy resources.^{1,2} The past few decades have seen great efforts to develop highly active HER catalysts under acidic conditions to replace the traditional precious Pt metal.^{3,4} While nanostructuring⁵⁻⁷ is a common approach to improve the activity considering that a variety of surface sites may be exposed in nanomaterials, the catalyst recyclability, durability and longterm performance turn out to be problematic along this "activesite-by-nano" strategy.⁸⁻¹⁰ To replace Pt effectively, a more fundamental question is, therefore, whether there are bulk material catalysts that are competitive for the HER under acidic conditions. This would involve the design of the bulk and surface electronic structure to optimize the H adsorption and



Fig. 1 (a and b) DFT results for Pd–B alloy formation energy convex hull and hcp Pd_2B crystal.²² (c) Schematic representation of the synthetic route for Pd₂B NS/C. (d) HRTEM image of Pd₂B NS. The inset is the magnified image of the rectangular region in (d). (e) STEM image and STEM-EDS element mapping Pd₂B. (f) XRD patterns illustrating the phase transformation from Pd (fcc) to Pd₂B (hcp) at different reaction temperatures. Gray line: simulated XRD pattern of the hcp phase.

the subsequent HER on the surfaces,^{9,11} which remains highly challenging to the current knowledgebase.

Encouraging progress has been made recently by alloying transition metals (Pd, Ru, Ir, Ag, Ni, Co) with other main group elements, such as P¹²⁻¹⁷ and S.¹⁸⁻²⁰ But, due to the difficulty in the synthesis and the lack of knowledge on the phase diagram, it has been challenging to identify new catalysts with better activity and stability than Pt metal. Guided by the first principles global optimization technique,²¹ our recent study²² showed that Pd-B can form a stable bulk alloy (as indicated by the convex hull in Fig. 1a) and the thermodynamically most stable Pd boride phase is a hcp Pd₂B phase (see atomic structure in Fig. 1b, B locates at the octahedral (Oh) interstitial sites of Pd lattice), which is further predicted to exhibit a much higher intrinsic HER activity than Pt. To prove this, the pure hcp Pd₂B phase with a high surface area needs to be synthesized. Previous attempts to alloy Pd with B generally can only reach low B contents (<20%),²³⁻²⁶ as reflected by the characteristic fcc Pd lattice from X-ray diffraction (XRD). A recent synthetic work reports poly(vinylpyrrolidone) (PVP) coated Pd-B nanocrystals with a higher B content (\sim 35%),²⁷ but no activity was measured for catalytic reactions.

Here we report a new synthetic procedure to produce Pd_2B nanosheets (NS), which achieves a low overpotential HER catalyst, 15.3 mV at 10 mA cm⁻², a small Tafel slope of 22.5 mV dec⁻¹

and a high exchange current density (j_0) of 2.84 mA cm⁻². The Pd₂B activity is much higher than that of Pt/C $(j_0 = 0.92 \text{ mA cm}^{-2})$, indicating a superior intrinsic electrocatalytic activity. And the Pd₂B NS/C catalyst has a good durability in acidic HER, retaining 97.6% activity after working at a constant potential with the initial $j = 10 \text{ mA cm}^{-2}$ for 12 h. Our synthetic approach is simple and time-saving, involving a solvothermal reaction process to efficiently speed up the fcc-to-hcp phase transition and the subsequent insertion of B into the Pd lattice, which is found to be the rate-determining step in Pd₂B synthesis. The produced Pd₂B NS/C catalyst has a large electrochemically active surface area, 24.6 m² per 1 g Pd.

Results and discussion

Synthesis and structural characterization of Pd₂B NS/C

Specifically, our two-step synthesis method is schematically shown in Fig. 1c. First, Pd^{II} acetylacetonate ($Pd(acac)_2$, 300.0 mg), cetyltrimethylammonium bromide (185 mg), PVP (MW = 30 000, 960 mg), and Vulcan XC-72R Carbon (C, 104.1 mg) were mixed together with 2-phenylethanol (60 mL) in a 100 mL round-bottomed flask under an atmosphere of CO (100 mL min⁻¹) at 100 °C for 3 h. The Pd NS/C was obtained by centrifugation and washed with ethanol–acetone mixture (see ESI,† Fig. S1 for the

characterization of Pd NS/C). Then, Pd NS/C (30 mg), an excessive amount of dimethylamine borane (DMAB, Me₂NH·BH₃, 295 mg) and 5 mL THF are added into a sealed 10 mL Teflonlined stainless autoclave, with continuous stirring and reacted for 2 h at various temperatures (70, 90 and 120 °C). The final products of Pd_xB NS/C were filtered and subsequently washed with THF and ethanol several times.

Our synthetic method differs from the previously reported method²⁷ in that (i) nanosheet Pd is utilized as the precursor for metal boride; (ii) DMAB reagent acts as the efficient boron provider; (iii) high temperature (up to 120 °C) and high pressure (sealed in autoclave) solvothermal conditions are operated in B insertion process. All these measures greatly expedite the insertion of B kinetics, which leads to the formation of Pd_xB crystals within two hours. While the presence of PVP stabilizes the nascent Pd nanosheets, we found that PVP with suitable MW (30 000 in this work) is critical for achieving a highly active Pd_xB catalyst, which needs to be removable at the catalyst preparation stage (*i.e.* during centrifugation and washed with ethanol–acetone mixture before B insertion). Similar reaction conditions using the previous synthetic method²⁷ do not yield a Pd_xB catalyst with a high HER activity (see ESI,† Fig. S2).

Fig. 1d-f demonstrates the experimental characterization of the synthesized hcp structure of Pd₂B crystal (120 °C), as confirmed by high-resolution transmission electron microscopy (HR-TEM), the scanning TEM-energy dispersive X-ray spectroscopy (STEM-EDS) element mapping and XRD. The Pd₂B NS are highly dispersed on the C (see SEM and TEM images in ESI,† Fig. S3a and b). Fig. 1d shows the hcp lattice for the Pd₂B from HR-TEM. The inset is a magnified image of the rectangular region in (d), which highlights the characteristic ABAB hcp stacking of Pd atoms (the bright dots). The distances between the characteristic (100) and (002) planes (for convenience all the lattice planes in Miller index hereafter referred to the hcp Pd sublattice in Pd₂B crystal) are measured to be 2.64 Å and 4.88 Å, respectively, which agrees well with the theoretical values of Pd₂B crystals (2.65 Å and 4.77 Å). The electron diffraction pattern images (in ESI,† Fig. S3c) also confirm the hcp lattice of Pd₂B. Fig. 1e shows the STEM-EDS element mapping of Pd₂B NS/C. We found that the Pd and B elements spread uniformly on C supports, confirming the Pd-B alloy formation and no appreciable nanostructures of B solid and Pd metal formation. Additionally, the energy dispersive X-ray (EDX) spectrum reveals that the atomic ratio of Pd:B is estimated to be 21.3:12.5 (ESI,† Fig. S3d and Table S1), which is indeed close to the 2:1 theoretical value.

The XRD in Fig. 1f shows how the hcp Pd_2B phase evolves from pure Pd, which is recorded for samples synthesized with different reaction temperatures, *i.e.* 70 °C, 90 °C and 120 °C. The hcp lattice appears as early as in the 90 °C sample, and it is not until 120 °C that the fcc lattice disappears completely. The characteristic peaks for the hcp lattice shown in the 120 °C sample are 2θ = 36.50 (100), 37.950 (002), 41.30 (101), 53.65 (102), 65.65 (110), 70.80 (103), 78.40 (112) and 80.60 (021) degree which corresponds to a hcp lattice with *a* = 2.84 Å and *c* = 4.74 Å. We note that from Pd NS/C to Pd_xB NS/C (70 °C), the fcc lattice (111) peak down shifts from 39.95 to 38.79 degrees, which suggests the expansion of the Pd lattice by ~2.90%, presumably due to the insertion of B. From our calculations,²² the lattice parameters for Pd₅B (still has the fcc Pd sublattice) are a = 5.03 Å, b = 5.75 Å, c = 6.49 Å, $\alpha = 77.83^{\circ}$, $\beta = 75.16^{\circ}$, $\gamma = 72.47^{\circ}$, where the fcc (111) distance is 3.1% larger than that in Pd metal. These results provide direct evidence that the insertion of B is slow and accompanied by the expansion of the Pd lattice and a fcc-to-hcp transition.

The electronic structures of the Pd_xB samples have also been characterized by using magnetic susceptibility. The magnetic susceptibility of all Pd_xB samples is measured in the temperature interval between 300 and 2 K in a magnetic field of 1 T, as displayed in ESI,† Fig. S4. We found that with the increase of B content, the susceptibility drops sharply. While pure Pd metal has a large magnetic susceptibility due to free d electrons, the Pd₂B (120 °C sample) transforms largely to a diamagnetic magnetization material. This suggests that Pd forms a strong covalent bond with B that leads to the low susceptibility of d magnetism under a magnetic field.²⁷ From our first principles DFT calculations (all calculation setups can be found in the ESI[†]), the Pd₂B d band has a much reduced density of states (DOS) close to the Fermi level compared to that in the Pd d band, see ESI,† Fig. S5a. As a result, the d band center for Pd₂B (-3.2 eV) is lower compared to that for Pd (-2.2 eV). Despite the reduced DOS in Pd₂B, it also shows that both Pd and Pd₂B are metallic and the valence band maximum should be similar. Indeed, we have performed ultraviolet photoelectron spectroscopy (UPS) for Pd NS/C and Pd2B NS/C samples, as shown in ESI,† Fig. S5b and found that the two samples have similar cut-off values, i.e. 16.66 eV (Pd NS/C) and 16.68 eV (Pd2B NS/C), and a similar work function, i.e. 4.60 eV (Pd NS/C) and 4.58 eV (Pd₂B NS/C). The similarity shown in the UPS may also be due to the presence of a large amount of carbon in both samples.

In order to better understand the surface electronic states of Pd₂B NS/C, we have performed X-ray photoelectron spectroscopy (XPS) for the Pd and Pd_xB composites. The results are detailed in the ESI,† Fig. S6 and they are summarized below. The survey scan of Pd₂B NS/C (ESI,† Fig. S6a) clearly indicates the presence of carbon (C), palladium (Pd) and boron (B) atoms. The Pd 3d_{3/2} level binding energy is 340.6 eV for Pd NS/C and shifts to a higher binding energy of \sim 341.0 eV for Pd₂B NS/C (ESI,[†] Fig. S6b). The further detailed XPS analysis for Pd₂B NS/C (ESI,† Fig. S6c) shows that each of the two Pd 3d_{5/2} and Pd 3d_{3/2} peaks can be fitted into two small peaks, suggesting the dominance of Pd⁰ at 335.4 and 340.8 eV (335.4 and 340.7 eV for pure Pd in literatures²⁸) and the presence of minority Pd²⁺ at 336.1 and 342.3 eV. The presence of Pd²⁺ appears to be intrinsic to Pd samples prepared in air due to the surface adsorbed O species. On the other hand, the B 1s level (ESI,† Fig. S6d) peaks mainly at 187.8 eV, indicate the presence of B⁰, while a minority peak occurs at 192.2 eV corresponding to B^{3+} possibly due to the surface B_2O_3 oxide impurity. From the XPS spectrum, it is clear that the B atoms exist primarily in the reduction state, forming an alloy with Pd.

Electrochemical characterizations. Now we are at the position to evaluate the electrochemical HER performance of Pd_2B



Fig. 2 (a) Polarization curves of Pd NS/C, Pd_xB NS/C and commercial Pt/C in 0.5 M H_2SO_4 at a scan rate of 1 mV s⁻¹. (b) Polarization curves normalized by ECSA. (c) Comparison of HER specific activity of Pd NS/C, Pt/C and Pd₂B NS/C at 50 mV overpotential. (d) Measured overpotentials for Pd₂B NS/C and other reported catalysts in acidic solutions. (e) HER Tafel plots. (f) *i*-*t* curves for Pd, Pt and Pd₂B catalysts at constant potential with the initial *j* of 10 mA cm⁻² for 12 h.

NS/C. Linear sweep voltammogram (LSV) is conducted for the precursor Pd, commercial Pt/C and Pd_xB NS/C in N₂-saturated 0.5 M H₂SO₄ solutions with a typical three-electrode setup at room temperature. The potentials reported in our work were referenced to the reversible hydrogen electrode (RHE) (*E*(V vs. RHE) = *E*(V vs. SCE) + 0.255 V. The reference electrode has been calibrated carefully, see ESI,† Fig. S7). The electrochemically active surface area (ECSA) was measured for all catalysts, which were determined by the CO stripping experiment (see ESI,† Fig. S8). Based on the CO oxidation region in the first scan of the as-prepared catalyst, the ECSA values for Pd NS/C, Pd_xB NS/C (90 °C), Pd₂B NS/C (120 °C) and Pt/C are calculated as 44.0, 37.8, 23.6, 24.6 and 39.6 m² g⁻¹, respectively.

As shown in Fig. 2a, the Pd₂B NS/C shows a nearly zero onset overpotential ($\eta = 1.3 \text{ mV}$, $j = 1.0 \text{ mA cm}^{-2}$), and 15.3 mV overpotential at $i = 10 \text{ mA cm}^{-2}$, which is 14.8 mV less than that of commercial Pt/C (30.1 mV). The specific activity (SA) normalized by ECSA in Fig. 2b shows that Pd₂B NS/C exhibits excellent electrocatalytic activity toward HER compared to other catalysts. At the overpotential of 50 mV (Fig. 2c), Pd₂B NS/C exhibits the SA of 9.41 mA $\text{cm}_{\text{Pd}}^{-2}$, which is 2 times that of Pt/C (4.45 mA $\text{cm}_{\text{Pt}}^{-2}$), and much higher than that of Pd NS/C. For comparison, we also list the previously reported overpotential for the high activity HER catalysts in Fig. 2d $^{10,28-31}$ and Table S2 (ESI†). For example, the most active non-Pt transition metal catalysts, Ru/CN²⁹ (22.0 mV), and Au@PdAg NRBs³⁰ (26.2 mV), are both less active than the Pd₂B sample. It should be mentioned that we also noticed that with the increase of B content, the Pd_xB becomes more and more active: the overpotentials at the *j* of 10 mA cm⁻² for Pd NS/C, Pd_rB NS/C (70 °C) and Pd_rB NS/C (90 °C) are 65.2, 31.5 and 20.6 mV, respectively (ESI,† Fig. S9). This supports the high electrocatalytic activity for the Pd–B alloy and the unique catalytic role of B in the Pd lattice.

The HER kinetics of Pd_xB catalysts are also measured by using the Tafel plots and the results are compared with Pt/C catalysts. The Tafel slope (Fig. 2e) of Pd_2B NS/C is 22.5 mV dec⁻¹, which is lower than that of Pd NS/C, Pd_xB NS/C (70 °C), Pd_xB NS/C (90 °C) and Pt/C (75.5, 45.4, 34.4 and 30.4 mV dec⁻¹ respectively). The small Tafel slope for Pd_2B NS/C leads to a high exchange current density (j_0) of 2.84 mA cm⁻² as calculated by the Butler–Volmer equation (ESI,† Fig. S10). This value is also obviously larger than that of the commercial Pt/C catalysts, 0.92 mA cm⁻² (the value varies from 0.5–1.5^{10,32} in different literatures), and comparable with the Ru/CN catalyst (1.9 mA cm⁻²) reported recently.²⁹

Importantly, Pd₂B NS/C, as a bulk material catalyst, also possess a high durability (Fig. 2f): the HER activity remains 97.6% after 12 h, indicating a good lifetime for the HER. For comparison, the Pd NS/C and commercial Pt/C HER activity remains only 39.9% and 68.7% after 12 h, suggesting the dramatic change of catalyst morphology and active site structure after the reaction. Indeed, the hcp phase in Pd₂B remains after 12 h reaction, as revealed from the XRD analysis of the catalyst after the reaction (see ESI,† Fig. S11). Furthermore, an accelerated durability test was performed for the Pd₂B NS/C catalyst. After repeated cycling in the range from 0.05 to -0.065 V vs. the RHE for 1000 cycles in 0.5 M H₂SO₄ at a scan rate of 100 mV s^{-1} , we found that the polarization curve for Pd₂B NS/C only shifts negligibly, as shown in ESI,† Fig. S12a, confirming that the catalyst is stable in typical HER working conditions. In addition, the service life of the electrode was estimated through an accelerated service-life test, polarizing

the electrode at a large current condition (500 mA cm⁻²). The service life for Pd₂B NS/C with a current density of 10 mA cm⁻² is estimated to be ~2.9 years (see ESI,† Fig. S12b for details).

From Fig. 2, we can see that the formation of the hcp phase further enhances the HER activity and the catalyst stability. This is presumably due to the fact that the Pd₂B bulk is the thermodynamically most stable phase in the Pd–B alloying diagram and only at this B-saturated phase the catalyst becomes fully resistant to H-corrosion. As shown in ESI,† Fig. S13, we found that while the polarization curves of Pd NS/C show the typical large Pd–H underpotential absorption at 25.2 mV, an increase in the content of B helps to reduce the underpotential peak, which is completely removed in Pd₂B. Therefore, it is important to understand how the hcp phase evolves during the synthesis of the catalyst, which could be of general significance for synthesizing metal boride catalysts.

Mechanism of B insertion into Pd. To this end, we have first compared the diffusion pathway of the B atom into Pd and Pd₂B lattice by using DFT calculations (also see ESI⁺ for details). All the pathways were searched using LASP software developed in our group.³³ In both pure Pd and Pd₂B, the bulk B atom prefers to sit in the O_h interstitial site, forming a B-Pd₆ structural unit, and the B atom at the T_d interstitial site is highly unstable (>1.44 eV in Pd; 0.69 eV in Pd_2B). For a single B atom diffusion (see Fig. 3a), we found that the diffusion in the hcp Pd₂B lattice (from one vacant O_h site to another) is facile with the barrier as low as 0.55 eV, which is much lower than that for B diffusion (1.69 eV) in a pure Pd lattice. This can be attributed to two factors, *i.e.* (i) the lattice difference between the fcc and hcp lattice: the diffusion of a B atom from one O_h interstitial site to another needs to bypass a tetrahedral (T_d) interstitial site in the fcc lattice, but this is no longer required

B diffusion in bulk

Surface Pd_B formation

Fig. 3 (a) Reaction profiles and the key structures of B diffusion in Pd and Pd_2B bulk. (b) Reaction profiles of surface Pd_2B formation. The snapshots for the initial states (ISs), transition states (TSs) and final states (FSs) were shown on the right. The transferring B atoms are highlighted as orange balls.

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in the hcp Pd_2B . (ii) The lattice expansion of Pd_2B : its lattice expands by ~9% compared with pure Pd, which helps to stabilize the transition state (TS) in diffusion. The low barrier of B diffusion in the Pd_2B lattice implies that the B diffusion can be significantly facilitated after the fcc-to-hcp phase transition. With this information on a single B atom diffusion, we have proposed the following B insertion pathway, see Fig. 3, and it is verified by DFT calculations and experimental observations, as elaborated below.

Firstly, starting from pure Pd (state 1 in Fig. 3b), the surface B diffuses into the O_h site in the sublayer of Pd (state 2). The reaction is strongly exothermic (1.35 eV) with a low barrier (0.32 eV). Next, more B atoms can diffuse into the subsurface Oh site until the sublayer B contents reaches to 0.5 monolayer (ML) (state 3), which is strongly exothermic by 2.98 eV. Further diffusion of B into the deeper bulk layers of the fcc lattice is however kinetically hindered, with the calculated barrier up to 1.56 eV, as shown in the reaction profile from state 3 to state 5 (the structures of TS3 and state 5 can be found in ESI,† Fig. S14). Therefore, the fcc-to-hcp transition has to start immediately from the surface layers after the sublayer B content reaches to 0.5 ML. Secondly, the fcc-to-hcp transition for the surface layer occurs with a barrier of 0.058 eV per Pd in the layer, where the top two Pd layers slip towards $[11\overline{2}]$ by 1/3 lattice constant (state 4). This step results in the formation of the hcp Pd₂B overlayer, which eventually leads to the lattice expansion of the surface layers up to \sim 9%. Thirdly, after the fcc-to-hcp phase transition, the subsurface B will further diffuse into the deeper bulk layers (state 6), which is kinetically feasible with the barrier 0.66 eV. Finally, additional B atoms are able to refill into the vacant O_h interstitial site at the subsurface layer and restore the B contents to 0.5 ML (state 7).

The overall barrier for the B insertion process is 0.88 eV, which is much lower than that without the fcc-to-hcp phase transition (1.56 eV). The mechanism, the insertion of B accompanied by the layer-by-layer Pd lattice phase transition, is consistent with the experimental XRD observation that the hcp phase can be detected as early as in the 90 $^{\circ}$ C samples but the hcp phase crystallization completes at 120 $^{\circ}$ C.

HER catalytic kinetics. Considering the stepwise formation of Pd₂B from Pd metal, it is of interest for us to examine whether the Pd₂B composition is critical to the high HER activity, or alternatively speaking, at what stage the HER activity is substantially enhanced. This information is important for understanding the active site in the Pd₂B NS/C catalyst. For this purpose, we have selected five different models from the lowest energy pathway in Fig. 3, namely, pure Pd metal (state 1), state 3 (fcc Pd lattice with 0.5 ML subsurface B), state 4 (fcc Pd lattice with only the first layer sliding to hcp phase and 0.5 ML subsurface B), and Pd₂B with 50% B content being removed (i.e. Pd2B-50%) and Pd2B. We compared the HER activity of the close-packed surfaces ((111) surface in the fcc lattice and (001) surface in the hcp lattice) of these five systems for the Tafel mechanism, surface H coupling reaction $H^* + H^* \rightarrow$ H_2 , which is known to be the major pathway for the HER on active metals.²²

а

Energy (eV)

b

0

Energy (eV)

Pd

TS

69 eV

FS

With phase transition

out phase transiti





Fig. 4 (a) The free energy reaction profiles of H–H coupling on different surfaces. (b) The structures of the transition states. Both the top and the side views of each TS are shown. The ΔG_a are indicated at the right bottom corners. Pd: cyan balls; B: pink balls; H: white balls, and the reacting H atoms are highlighted as lite cyan balls.

To study the Tafel reaction of the HER, one needs to know first the equilibrium surface H coverage under reaction conditions, where the adsorbed H equilibrates with the solvated protons in the electrolyte. This can be done by determining the H adsorption free energy ($\Delta G_{\rm H}$) using the DFT calculations, as utilized in our recent theoretical study.²² We found that the surface H coverage is 1 ML on Pd(111), but it drops to 0.25–0.50 ML on the other surfaces with 0.5 ML subsurface B. In all cases, the adsorbed H prefers to adsorb at the three-fold hollow site, where no subsurface B is present directly beneath the hollow site since a too-close contact (<2 Å) between H and B is thermodynamically prohibited (H adsorption energetics on different surface sites can be found in ESI,† Fig. S15).

Next, we examine the kinetics of two surface H coupling to form a H₂ molecule on these surfaces. Fig. 4a and b show the free energy reaction profiles and the located TS structures. The reaction occurs by following a two-step mechanism, namely, first the Volmer step and then the Tafel step. We always start from the equilibrium H coverage condition for the surface as determined by thermodynamics. The Volmer step occurs first with one proton from the solution to adsorb on the surface with the simultaneous electron transfer: $* + H^+ + e^- \rightarrow H^*$. Next, this additional H reacts with the nearby surface H to achieve the TS, which is a Tafel step: $H^* + H^* \rightarrow H_2$. We found that the TS is a [H-H] complex nearby a top site with the H-H distance in the range of 0.81-1.13 Å. Despite the same reaction mechanism, the free energy profiles for these surfaces are markedly different. As shown in Fig. 4a, the free energy barrier (ΔG_a) for the HER on Pd(111) is 0.95 eV, which is very close to the previously reported barrier on Pt(111).³⁴ The TS of H-H coupling is over the fcc hollow site. The $\Delta G_{\rm a}$ then reduces to 0.64 eV and 0.60 eV at state 3 and state 4 surfaces, respectively. In both cases, the TS is achieved with one H being at the fcc site and another H being near the bridge site (see Fig. 4b).

After the fcc Pd lattice is fully transformed to the Pd_2B hcp lattice, we found that the free energy barrier drops again to 0.49 eV, the value being very close for Pd_2B -50% and Pd_2B (0.52 and 0.49 eV). In both the cases, the TS is achieved over the fcc hollow site. We note that the H–H distance of the reacting Hs at TSs on the close-packed Pd_2B (001) is 1.03 Å, being much longer

than that (0.82 Å) on Pd (111). This suggests an early TS, *i.e.* structurally being close to the initial state (IS), for the HER on Pd₂B, supporting the low barrier in Pd₂B.

Our results indicate that the enhancement of B to HER starts as early as the presence of the first layer B. The further enhancement of activity requires the presence of hcp Pd_2B lattice. With the presence of hcp Pd_2B lattice, the exact B concentration becomes not critical, and even 50% B in the Pd_2B lattice would lead to the similar high activity of the catalyst. From these results, we can summarize the dual roles of B in the activity enhancement: (i) the presence of the subsurface B can locally weaken the H–Pd bonding and facilitate the H–H coupling; (ii) the lattice expansion after the hcp lattice formation will further promote the H–H coupling, where the H adsorption at the three-fold hollow sites at the IS is more weakened compared to the TS [H–H] complex.

Conclusions

This work develops a new synthetic method for synthesizing a Pd₂B crystal and further demonstrates its HER superactivity and high stability under strong acidic conditions. The step-wise structure evolution from metal Pd to metal boride Pd₂B is analyzed by theoretical calculations, which shows that the phase transition is critical to the B insertion kinetics. The high HER activity of the Pd2B catalyst is explained by the presence of subsurface B and the expansion of the Pd lattice. As Pd₂B bulk alloy is the global minimum for the Pd-B alloy as predicted by theory, the success in experiment synthesis opens the possibilities for this stable phase as an active catalyst, in particular for hydrogenation catalytic reactions. Considering the lower overpotential of Pd₂B than Pt in the HER, it is expected that the highalloying transition metal boride may represent a class of high durability and high activity catalysts under harsh (e.g. reductive, acidic) conditions and thus deserve further exploration.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the National Key Research and Development Program of China (2018YFA0208600), the National Natural Science Foundation of China (21533001, 91745201, 21603165, 21573149), Shanghai Sailing Program (16YF1412300) and Fundamental Research Funds for the Central Universities. The authors thank Prof. Renchao Che, Dr Jie Zhang, and Dr Songhai Xie for the UPS and EDX measurements and helpful discussions.

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