

Intermetallic ZrPd₃-Embedded Nanoporous ZrC as an Efficient and Stable Catalyst of the Suzuki Cross-Coupling Reaction

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reactions at room temperature. Because a low Pd content (1 wt %) is sufficient to produce highly catalytically active Pd–ZrC, this material represents a great improvement in terms of Pd-atom economy over previously reported catalysts. Moreover, no catalytic degradation was noted over up to the presented 15 reaction cycles as the active Pd sites were stabilized in the ZrPd₃ lattice. These results indicate that Pd–ZrC has the advantages of both metal-loaded and intermetallic catalysts, providing an approach to enhance the degree of freedom for designing heterogeneous catalysts.

KEYWORDS: nanoporous materials, nanoparticles, intermetallic catalysis, heterogeneous catalysis, Suzuki cross-coupling reaction

■ INTRODUCTION

The Pd-catalyzed Suzuki cross-coupling reaction draws considerable research attention because it is one of the most practical approaches to realizing C-C bond formation.¹⁻³ Although Pd-based homogeneous species were originally investigated as catalysts of the reaction, the use of uncollectible Pd species and electron-donating ligands such as phosphines has raised environmental concerns over time.⁴ As a result, Pdloaded heterogeneous catalysts have been increasingly attracting attention as they can be easily separated from the solvent and reused.⁵⁻⁸ In the previous studies, most of the heterogeneous catalysts were investigated to enhance Pd dispersion. A high-surface area support combined with Pd, such as Pd@SiO₂,⁹ Pd/TiO₂,¹⁰ and Pd/CNT (carbon nanotube),¹¹ was thus focused, aiming to enhance the exposed Pd sites. Oxide- and carbon-based materials are typically employed, and their surface areas reached $300-750 \text{ m}^2 \text{ g}^{-1}$, with a few nm-sized Pd nanoparticles (NPs).⁹⁻¹⁴ Single-atom catalysts, such as Pd-ECN, are one of the extreme examples based on the material design concept described above.¹⁵ However, these heterogeneous catalysts are based on a simple combination of active metals (such as Pd and Au-Pd) and inert supports (carbon and oxides). Their active sites are susceptible to leaching and/or aggregation, resulting in a

Pd-ZrC achieved high catalytic performance in Suzuki cross-coupling

serious degradation of the catalytic performance within a few cycles (Figure S1a).^{6,13} Furthermore, as a result of the weak interactions between Pd and the supports, electron-rich Pd active sites are difficult to realize. Harsh reaction conditions, such as flux temperature¹⁰⁻¹⁴ and light irradiation,^{16,17} are thus needed to overcome the substrates' activation barrier.

Recently, Pd-based intermetallic catalysts such as Y–Pd binary systems have been reported as a possible solution to the issues described above.¹⁸ Different from the case of metalloaded systems, they work as catalysts in the absence of a support. Pd atoms are incorporated into intermetallic lattices, realizing Pd active sites that are both electron-rich and stable. Together with the low-work function nature, the catalytic activity and durability of these species have been shown to be superior to those of traditional metal-loaded systems.¹⁸ However, owing to the necessity to employ high temperatures to achieve their preparation, the surface areas of these catalysts

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Figure 1. Synthesis and characterization of nanoporous ZrC. (a) Representation of the crystal structure of ZrC, which is an NaCl-type structure. (b) Schematic illustration of the synthesis of ZrC precursors (PZSA). (c) Powder X-ray diffraction (XRD) patterns of the t-ZrO₂-C composite after heat treatment (first at 900 °C and then at 1400 °C). The simulated XRD patterns of t-ZrO₂ and ZrC were also shown respectively. (d,e) High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images of t-ZrO₂-C. (f) Representation of the structure of the generated t-ZrO₂-C. (g,h) HAADF-STEM images of ZrC NPs. (i) Representation of the nanoporous structure of the generated ZrC NPs.

are limited to a few $m^2 g^{-1}$, so the vast majority of Pd sites are not exposed (Figure S1b). These practical constraints result in species characterized by a low Pd-atom economy. Therefore, the use of intermetallic catalysts has remained confined to a relatively narrow range of practical applications. The combination of the features of intermetallic and metal-loaded catalysts, which would allow nanometer-sized particles of intermetallic species to disperse on supports of high surface areas, has thus become an increasingly important research goal.

In this context, we have focused on ZrC NPs as a candidate of the support. They are metallic materials with a low-work function feature ($\Phi_{WF} = 3.7 \text{ eV}$).^{19,20} Although ZrC can be synthesized by calcining a Zr organic polymer (polyzirconosaal, PZSA), this approach did not result in noticeable particle aggregation.²¹ The robustness with respect to high temperatures allows intermetallic catalysts to grow on the surface of ZrC without decreasing its surface area. Moreover, the fact that Zr has a lower value for electronegativity (1.33) than Pd (2.20) is a quite advantageous feature from the standpoint of realizing electron-rich Pd active sites.²² We were therefore inspired to combine Zr–Pd intermetallic compounds with ZrC NPs for a new type of heterogeneous catalyst to be utilized in the Suzuki cross-coupling reaction (Figure S1c).

Herein, we report the synthesis of Pd–ZrC, a material in which NPs of the intermetallic ZrPd₃ compound are created on the surface of nanoporous ZrC NPs. We also describe the use of this material as an efficient and stable catalyst of the Suzuki cross-coupling reactions. Because ZrPd₃ and ZrC share the same cation, Pd–ZrC was synthesized by simply calcining PZSA and Pd acetate. Using this approach, we found that nanoporous structures were generated *in situ* on ZrC NPs, realizing a support characterized by a high surface area (444 m² g⁻¹). The particle sizes of generated ZrPd₃ are around 2–4 nm, and as a result, more exposed Pd active sites were present in the obtained material than in the previously reported Y–Pd intermetallic catalysts despite the fact that a much lower amount of Pd (1 wt %) was used to produce Pd–ZrC. Importantly, because the Pd sites are negatively charged and

Pd–ZrC has a strong electron-donating ability, high catalytic performance for the Suzuki cross-coupling reaction was achieved at room temperature. For this catalyst, the calculated turnover frequency (TOF) was as high as 2943 h⁻¹, vastly surpassing the values reported for commercial catalysts such as Pd/C (TOF = 193 h⁻¹). Moreover, the catalytic activity of Pd–ZrC was not degraded even after 15 reaction cycles because the Pd active sites are stabilized by the lattice framework of ZrPd₃. These observations prove the effectiveness of combining intermetallic catalysts with supports as an approach to improve the activity, durability, and atom economy of noble metal-based catalysts.

RESULTS AND DISCUSSION

In Figure 1a,b, a schematic representation of the crystal structure of ZrC and the synthetic procedure implemented to obtain this support are illustrated. In this study, we employed PZSA as a precursor for ZrC synthesis. When PZSA was sintered at 900 °C under an Ar gas flow, it underwent pyrolytic decomposition, transforming into tetragonal ZrO₂ (t-ZrO₂; see Figure 1c). Although the peaks arising from carbon compounds could not be observed in the powder XRD plots, the obtained powder is black, suggesting the presence of amorphous carbon (Figure 1c). Indeed, HAADF-STEM analysis confirmed the presence of amorphous carbon phases located between t-ZrO₂ particles to form the t-ZrO₂-C composite (Figure 1d-f). The carbon content was estimated to be 32 wt % for t-ZrO2-C on the basis of TG-DTA measurement (Figure S2a). As the calcination temperature is increased up to 1400 °C, t-ZrO₂ was reduced by carbon, and the composite transformed into ZrC NPs (Figure 1c,g-i).

Interestingly, the surface area of the obtained ZrC NPs is enhanced from 196 m² g⁻¹ (t-ZrO₂-C) to 339 m² g⁻¹ (ZrC), which is far greater than the value (~10 m² g⁻¹) estimated simply on the basis of the ZrC particle size (Figure S2c,d). The plot obtained from an N₂ adsorption/desorption experiment conducted on ZrC NPs was characterized by the presence of a distinct hysteresis, demonstrating that a structure comprising



Figure 2. (a) Synthetic procedure of Pd–ZrC catalysts. (b,c) Powder XRD pattern of Pd–ZrC composites characterized by different Pd contents. The black solid circle indicates the Bragg peak positions of ZrPd₃. The calculated XRD patterns of ZrC and ZrPd₃ are also shown. (d) HAADF-STEM images of freshly prepared Pd(1 wt %)–ZrC. The generated ZrPd₃ phases appear as bright spots. At the right side of (d) is a representation of the crystal structure of ZrPd₃, with Zr and Pd atoms drawn as green and gray balls, respectively. A schematic representation of the structure of Pd–ZrC is also illustrated at the bottom section of (d). (e) Pd K-edge X-ray absorption near edge structure (XANES) of Pd in the ZrPd₃ plane and Pd migrated to Pd(1 wt %)–ZrC. The corresponding data for pure Pd and PdO are also reported in the plots as references for Pd⁰ and Pd²⁺. (f) EXAFS analysis of Pd–ZrC. The experimental data can be fitted by considering ZrPd₃ and its interaction with ZrC. The bonding lengths were estimated to be 2.81 Å for both Zr–Pd and Pd–Pd bonding and 2.21 Å for Pd–C bonding. Pd–C bonding is derived from the interaction between Pd of ZrPd₃ and C of ZrC. (g) X-ray photoemission spectroscopy (XPS) data of Pd–ZrC catalysts. The blue and green regions are derived from Zr 3p orbitals and Pd 3d orbitals, respectively. As emphasized in (h), the Pd peaks are shifted ~0.5 eV to lower binding energy compared with zero-valence Pd⁰ (reference: Pd/Al₂O₃), suggesting the presence of negatively charged Pd.

pores with a few nm in size had been generated, which, in turn, contributed to the enhancement of the material's surface area (Figure S2f). The pore volume of the obtained ZrC was estimated to be ~ 0.3 cm³ g⁻¹, corresponding to a porosity value of 67%. The porous structure of ZrC NPs was made evident by HAADF-STEM observations, which indicated the presence of pores with a few nanometers in size (Figure 1h). HAADF-STEM data also indicated the pore morphology to be consistent with that of the amorphous carbon present in t- ZrO_2-C_1 leading to the conclusion that the porous structure had been generated as a result of the emission of CO_r (Figure 1f,i). Notably, this method is also applicable to HfC to generate nanoporous structures (Figure S3a-c). However, despite the fact that HfC exhibits almost identical properties to ZrC, in this study, we focus on ZrC because Hf is much more expensive than Zr. Although we are aware that the synthesized ZrC NPs contain ~19 wt % of residual amorphous carbon (Figure S2b), it should be emphasized that the nanoporous structure is typical of ZrC itself, given that no hysteresis was observed in the N2 adsorption/desorption curve of the t- ZrO_2 -C composite (Figure S2c).

Encouraged by the high surface area of nanoporous ZrC NPs, we proceeded to calcine PZSA together with Pd acetate (Figure 2a). The major motivation for implementing this procedure was to obtain highly dispersed Zr–Pd intermetallic

phases in nanoporous ZrC NPs (Pd-ZrC), which is difficult to achieve using conventional solid-state or chemical reduction methods because of the strong oxygen affinity of Zr. In Figure 2b,c, the powder XRD data of Pd-ZrC prepared using different amounts of Pd are shown. As can be evinced from the data in the mentioned figures, as the amount of Pd in Pd-ZrC increased, a clear peak at $2\theta = 41.7^{\circ}$ can be identified. This signal is the main (20-20) peak of ZrPd₃, and its appearance confirms that intermetallic ZrPd₃ had been generated on the surface of ZrC. Meanwhile, the major peaks for Pd clusters, which should appear at $2\theta = 40.1$ (111) and 46.7° (200), could not be identified. This observation indicates that the formation of the ZrPd₃ intermetallic phase is favored under the implemented synthetic conditions over the formation of Pd clusters (Figure 2d). The high-resolution HAADF-STEM images and the results of energy-dispersive X-ray spectroscopy (EDS) analyses indicate that the ZrPd₃ is uniformly dispersed on the ZrC with a particle size of 2-4 nm (Figures S4,S5). The as-synthesized Pd-ZrC also displays a nanoporous structure, and in the case of Pd(1 wt %)-ZrC, the surface area is estimated to be 444 m² g⁻¹ (Figure S2e,g). As expected from the electronegativity gap between Zr

As expected from the electronegativity gap between Zr (1.33) and Pd (2.21),²² the Pd atoms are negatively charged, as confirmed by XANES. As can be evinced from the data reported in Figure 2e, the absorption edge for the Pd species of

both Pd(1 wt %)–ZrC and ZrPd₃ is characterized by a lower energy than their counterparts for elemental Pd (Pd⁰) and PdO (Pd²⁺). Moreover, the XPS data showed that the binding energy of Pd 3d peaks shifted ~0.5 eV to a lower binding energy region compared to zero-valence Pd⁰ of Pd/Al₂O₃ (Figures 2g,h and S6). These observations are consistent with the results of Bader charge analysis, in which Zr and Pd were calculated to be Zr^{1.2+} and Pd^{0.4-}.

The EXAFS data show that the bonding lengths of Zr-Pd and Pd-Pd are respectively 2.81 Å, consistent with the value of ZrPd₃ and slightly elongated than that of elemental Pd (2.74 Å) (Figure 2f, S7, S8 and Table S1). The contribution of Pd-C bonding with 2.21 Å length can also be detected in EXAFS spectra, which can be interpreted by the interaction of Pd of ZrPd₃ and C of ZrC. Because ZrPd₃ has two Pd sites, Pd₁-M and Pd_2-M (M = Zr, Pd) bondings are respectively summarized in the Table S1. The fitting results of EXAFS data show that the Pd-ZrC catalyst has a lower coordination number (CN = 7.02) than that of bulk $ZrPd_3$ (CN = 12) (Table S1). This may originate from the nanosize effect because the ZrPd₃ NPs (2-4 nm in diameter) have more exposed Pd sites that have less bonding. These data are consistent with the CO pulse chemisorption data (Table S2), revealing that ~ 0.01 and $\sim 3\%$ of used Pd are actually exposed for bulk ZrPd₃ and Pd-ZrC, respectively. Therefore, based on these experimentally and computationally obtained results, it is concluded that nanometer-sized ZrPd₃ is successfully generated on nanoporous ZrC and realized negatively charged Pd sites.

ZrC is a metallic material, and the value of its work function $(\Phi_{WF} = 3.7 \text{ eV})^{20}$ is smaller than that of ZrPd₃ ($\Phi_{WF} = 4.7 \text{ eV}$, calculated by DFT). Given that ZrC and the intermetallic ZrPd₃ species are electronically contacted, this characteristic feature should promote the electron-donating ability of Pd-ZrC, together with negatively charged Pd active sites. Moreover, the high surface area of Pd-ZrC's nanoporous structure increases the number of exposed Pd sites, which should improve the material's Pd-atom economy. We were thus motivated to investigate the use of Pd-ZrC as a catalyst of the Suzuki cross-coupling reaction. In detail, Pd(1 wt %)-ZrC displayed high catalytic performance, with a measured reaction rate of 7.3 mmol $g^{-1} h^{-1}$ at room temperature (25 °C) when iodobenzene and phenylboronic acid were used as substrates. The TOF value of the described reaction was estimated to be 2943 h⁻¹ based on the amount of exposed Pd sites in Pd(1 wt %)-ZrC. This TOF value is orders of magnitude larger than its counterparts reported for previously studied metal-loaded catalysts, even though the reaction conditions employed in the case of Pd(1 wt %)-ZrC are milder than those described in the literature (Tables S2 and S3).^{18,23-34} We also tested the catalytic performance of the bulk ZrPd3 powder for comparison. On the basis of the amount of surface-exposed Pd sites, the TOF value estimated for $ZrPd_3$ was as high as 2235 h⁻¹, a figure comparable to that calculated for Pd(1 wt %)-ZrC and far surpassing that reported for traditional Pd-loaded catalysts (Table S2).

The Suzuki cross-coupling reaction was also performed using bromobenzene and phenylboronic acid as substrates. Because C–Br has a stronger bond than C–I, the crosscoupling had to be performed at a higher temperature (60 °C), and in this case, the reaction rate was measured to be 9.3 mmol g^{-1} h⁻¹. The Pd–ZrC catalyst showed a lower activation barrier than Pd metal (Figure 3a,b). The apparent activation



Figure 3. Catalytic activity of the Pd–ZrC catalyst. Arrhenius plots of Suzuki cross-coupling reactions performed using (a) iodobenzene and (b) bromobenzene as substrates. Reaction conditions: 5 mg of Pd (1 wt %)–ZrC catalyst, 0.5 mmol organohalide, 0.8 mmol phenylboronic acid, 1.5 mmol K₂CO₃, and 5 mL of solvent. (c) Comparison between the recycle properties of Pd–ZrC and those of other Pd-based catalysts in the Suzuki cross-coupling reaction where iodobenzene is used as the reactant.

energies for the cross-coupling reactions catalyzed by Pd(1 wt %)–ZrC and those involving iodobenzene or bromobenzene as substrates were estimated to be 53 and 64 kJ mol⁻¹, respectively, which are 28 and 40% smaller than the values for Pd. These differences explain why the Pd(1 wt %)–ZrC-catalyzed reactions proceeded under milder conditions than the analogous reactions catalyzed by metallic Pd. As the oxidative addition of aryl halide is regarded as the rate-determining step of the Suzuki cross-coupling reaction,^{35,36} these related lower activation barriers can be ascribed to the weakening of the C–X (X = I and Br) bond achieved as a consequence of the strong electron-donating ability of Pd–ZrC, which will also be discussed later.

In addition to the high catalytic performance, a notable advantageous characteristic of Pd-ZrC is its stability over multiple reaction cycles. As can be evinced from the data in Figure 3c and Table S4, the Pd-ZrC catalyst can be recycled 15 times, and in terms of stability, Pd-ZrC vastly outperforms Pd-loaded ZrC (Pd/ZrC) and other well-studied Pd-loaded heterogeneous catalysts such as Pd/C, Pd/Al₂O₃, and Pb-Pd/ $CaCO_3$ (the Lindlar catalyst). For the cases of these competing catalysts, the catalytic activity starts to degrade within seven cycles. Such degradation can be attributed to the weakness of the interaction between the active Pd species and the supports, which results in progressive leaching and/or aggregation of the Pd sites. In contrast, in Pd-ZrC, the Pd active sites are anchored and stabilized in the crystal lattice of ZrPd₃. As a result, the island formation energy of ZrPd₃ became as high as 2.07 eV on the basis of DFT calculation, which is sufficiently large to prevent aggregation events (Figure S9). Furthermore, the stabilization energy of ZrPd3 on ZrC is ~2.9 eV per formula unit of $ZrPd_{3}$, within the model of a $Zr_8Pd_{24}-Zr_{72}C_{72}$ cluster. This value is large enough for preventing leaching of ZrPd₃ NPs.

Overall, these traits contribute to Pd–ZrC displaying a superior catalytic durability with respect to the other catalysts

Table 1. Data on Suzuki Cross-Coupling Reactions Involving Various Aryl Halides Catalyzed by Pd-ZrC^{*a,b*}



"Reaction conditions: 5 mg of catalyst, 0.5 mmol organohalide, 0.8 mmol arylboronic acid, 1.5 mmol K_2CO_3 , and 5 mL of solvent. Reaction temperatures were set to 25 °C for iodobenzene and 60 °C for bromobenzene. The yields given below the structure were determined using GC and GC–MS. ^bThe a part summarizes the reaction between various organohalides and arylboronic acids. The b part summarizes the reactions between organohalides and various arylboronic acids.

taken into consideration. Indeed, on the basis of the CO pulse chemisorption measurements, we confirmed that the amount of exposed Pd sites remains largely unchanged after the catalytic reaction, that is, the amount of adsorbed CO was measured to be 0.28 mL g^{-1} for the fresh catalyst and 0.23 mL g⁻¹ for the used one. HAADF-STEM analyses performed on the used Pd-ZrC catalyst also indicated that the sizes of the ZrPd₃ particles had remained largely unchanged after Pd-ZrC use (Figure S4). The negatively charged Pd was not affected for the used Pd-ZrC from the XPS data, demonstrating the robustness of the catalyst (Figure S10). Moreover, the concentration of dissolved Pd in the reaction solvent, corresponding to the 5th, 10th, and 15th cycles, was below the detection limit (<0.007 ppm) in inductively coupled plasma (ICP) spectroscopy analysis (Figure S11). All of the data on the used Pd-ZrC confirm the robustness of the Pd active sites toward leaching and aggregation, confirming the proposed rationale for the improved catalytic stability.

To investigate the wider applicability of Pd–ZrC as a catalyst of the Suzuki cross-coupling reaction, various substituted aryl halides and arylboronic acids were tested under standard reaction conditions. As shown in Table 1a, each of the tested iodobenzene and bromobenzene derivatives, characterized by the presence of a range of functional groups as substituents, could be converted to the corresponding coupled products in a high yield, regardless of whether the substituent

was an electron-donating or electron-withdrawing group (entry 1-15). Data confirming the feasibility and high yield of the coupling performed with different types of arylboronic acids are also listed in Table 1b (entry 16-25).

One of the key features of Pd–ZrC in the Suzuki crosscoupling reaction is the electron transfer effect toward the substrates. In Figure 4, representations of the adsorption of bromobenzene onto the surfaces of $ZrPd_3$ and Pd-ZrC are



Figure 4. Depictions of the electronic interaction between catalysts and bromobenzene. (a) Adsorption of bromobenzene on the $ZrPd_3$ (0001) plane. A view of the system from the top and C–Br bond lengths are shown at the bottom section of (a). (b) Same depictions and data as those for (a) but for the adsorption of bromobenzene on the surface of Pd–ZrC. The Zr and Pd atoms are represented as green and gray balls, respectively.

shown. The ZrPd₃ (0001) plane was employed in our model because it exhibits the lowest surface energy among the major planes of ZrPd₃ (Figure S9). As the reaction substrate approaches the ZrPd₃ (0001) plane, an electron transfer from ZrPd₃ to bromobenzene was identified, leading to the more negative charge of bromine and carbon atoms. According to the results of the Bader charge analysis, 0.05 e⁻ electrons was transferred to bromobenzene. Given that aryl halides have an electronic gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), the transferred electrons should be accommodated in the aryl halide's LUMO, which consists of the C–X σ^* antibonding orbital.³⁷ Consequently, the C–Br bond length undergoes 2.1% elongation as a result of the adsorption (Figure 4a).

The electron transfer effect can be boosted once $ZrPd_3$ species are generated on ZrC. In the Figure 4b we show the $ZrPd_3$ cluster stabilized on ZrC. According to the results of the Bader charge analysis, more electrons (0.11 e⁻) were transferred to bromobenzene, with a value comparable with the corresponding parameter reported for the Y_3Pd_2 catalyst (0.12 e⁻).¹⁸ Accordingly, in the case of the Pd–ZrC catalyst, the C–Br bond length was further elongated, explaining the suppressed activation energies of the Suzuki coupling reaction by the Pd–ZrC catalyst (Figure 4b).

These results show that not only the presence of a negative charge in the Pd sites but also the low value of the work function of ZrC enhances the catalytic activity. Indeed, the value of the surface TOF of Pd(1 wt %)-ZrC is 32% larger than that of the ZrPd₃ powder. Given that the value of the work function of ZrC $(\Phi_{WF} = 3.7 \text{ eV})^{20}$ is lower than that of $ZrPd_3$ (Φ_{WF} = 4.7 eV for the 0001 plane), as shown in Figure S9, the catalytic activity can be further boosted through electron donation from the catalyst to the substrates, a conclusion consistent with the results of the DFT analysis (see Figure 4). Moreover, the general tendencies with respect to the effectiveness of various catalysts are also supported by the trend in the values of the activation energy. The activation energy of the Suzuki cross-coupling reaction of iodobenzene had values of 53 kJ·mol⁻¹ for Pd-ZrC, 66 kJ·mol⁻¹ for the $ZrPd_3$, and 74 kJ·mol⁻¹ for the Pd metal (Figure S12), highlighting further the importance of both negatively charged Pd sites and the electronic interaction between ZrPd₃ and ZrC.

It should be noted that $ZrPd_3$ and elemental Pd host a similar structure if the most stable surfaces are considered, that is, the (0001) plane for $ZrPd_3$ and the (111) plane for Pd (Figure S8). It can be interpreted that one-fourth of Pd is replaced by Zr in $ZrPd_3$, and the local structure remained largely unchanged from the Pd metal. Although the bonding length is slightly elongated from Pd (2.74 Å) to $ZrPd_3$ (2.81 Å), this small geometric modification is unlikely to affect the reaction mechanism. Thus, a major improvement of catalytic activity should be derived from electron-rich Pd and the lowwork function nature of the ZrC support.

These experimental and computational results indicate that Pd–ZrC undergoes similar reaction mechanisms to Y_3Pd_2 catalysts for the Suzuki coupling reaction, showing the advantages of intermetallic catalysts to improve catalytic activity and stability. Different from Y_3Pd_2 , however, in Pd–ZrC, nanometer-sized ZrPd₃ particles are dispersed on the surface of nanoporous ZrC, allowing more Pd sites to be exposed. The TOF of Pd(1 wt %)–ZrC is comparable to that of Y_3Pd_2 if only exposed Pd was considered, while it becomes

orders of magnitude larger if total Pd sites are taken into account, much improving Pd-atom economy as the heterogeneous catalysts (Table S2).

Finally, we show that the Pd–ZrC catalyst can be applied to wider range of reactions, such as selective hydrogenation of nitroarenes, motivated by its strong electron-donating ability and the presence of negatively charged Pd active sites. As shown in Table S5, Pd–ZrC well catalyzes the reaction of hydrogenation of nitrobenzene even at room temperature (25 °C), which completes in 17 h. The reaction can be extended to various substrates with either electron-donating or -with-drawing functional groups. These results showed the wide versatility of Pd–ZrC and thus, the effectiveness of intermetallic phases as an efficient heterogeneous catalyst.

CONCLUSIONS

In summary, we successfully synthesized Pd-ZrC catalysts, in which nanometer-sized intermetallic ZrPd₃ is dispersed on nanoporous-structure ZrC, using simple and hazardous agentfree methods. The Pd-ZrC catalyst hosts negatively charged Pd, has a low-work function nature, and allows the Suzuki cross-coupling reaction to proceed with reduced activation energies. Despite much milder reaction conditions being employed, the measured TOF values surpass those reported for the traditional Pd-loaded catalysts. Moreover, Pd-ZrC does not display any significant degradation after up to 15 catalytic reaction cycles because the Pd sites are stabilized in the lattice framework of ZrPd₃. The remarkable stability and catalytic activity of this material, alongside the high Pd-atom economy it affords, cause Pd-ZrC to stand out among the heterogeneous catalysts of the Suzuki cross-coupling reaction. The results of the present study therefore highlight the importance of combining intermetallic catalysts and supports as a way to achieve multiple catalyst-improving objectives.

EXPERIMENTAL SECTION

Sample Preparation. Nanoporous ZrC was synthesized using a Zr organic polymer (PZSA). Typically, 6.40 g of ZrOCl₂·8H₂O and 1.55 g of salicyl alcohol were dissolved in 100 mL of methanol at 3 °C. A mixture of 2.0 g of acetylacetone and 4.04 g of triethylamine was then slowly added to the methanol solution while the reaction temperature was kept steady. Subsequently, the reaction mixture became turbid and it was allowed to warm to room temperature. After stirring for 4 h, the mixture was dried at 100 °C, upon which white solids were obtained. A total of 40 mL of THF was then used to extract the desired PZSA, and the obtained THF mixture was filtered to remove (solid) impurities such as triethylamine hydrochloride. After removing the solvent from the THF solution by drying at 100 °C, a light yellow PZSA powder was obtained. In order to obtain the ZrC phase, the PZSA powder was sintered at 1400 °C for 4 h under an argon flow in a tube furnace. Nanoporous HfC was also obtained simply by following the described procedure and stoichiometric ratios while replacing ZrOCl₂·8H₂O with HfOCl₂· 8H2O.

Pd–ZrC was prepared by sintering PZSA alongside Pd acetate. Notably, in order to increase the dispersion of Pd, both PZSA and Pd acetate were dissolved in acetone. The acetone solution was stirred for 1 h, and the solvent was subsequently fully vaporized at 100 °C. The obtained powder was then

transferred to a tube furnace and sintered at 1400 $^{\circ}\mathrm{C}$ for 4 h under an argon flow.

Sample Characterization. The obtained catalysts were analyzed using an X-ray powder diffractometer (D8-AD-VANCE, Bruker and MiniFlex, Rigaku) with a Cu K α radiation ($\lambda = 0.15418$ nm).

XPS measurements were conducted using ESCA-3200-(Shimadzu) with Mg K α radiation. The pressure of chamber is higher than 10⁻⁶ Pa, and 8 kV voltage was applied to the Xray source. A 4f_{7/2} peak (84.0 eV) of deposited Au was used as the reference during the measurements.³⁸

Nitrogen adsorption/desorption measurements were performed to estimate the Brunauer–Emmett–Teller surface area of the catalysts (BELSORP-mini II, BEL). The number of moles of exposed Pd sites found on the surface of the material was estimated by performing experimental measurements and formulating theoretical predictions. CO-pulse chemisorption (BELCAT-A, BEL) was measured at 50 °C using a He flow of 30 mL·min⁻¹ and pulses of 0.36 mL (9.88% CO in He). Prior to the analysis, the catalyst was treated with an Ar flow (50 mL·min⁻¹) at 400 °C for 30 min and then a He flow (50 mL· min⁻¹) at 400 °C for 15 min. To estimate the amount of exposed Pd, a value of 2 for the Pd/CO ratio was employed to infer the number of exposed Pd centers on the basis of the results of the CO pulse chemisorption experiment.

The morphology of the catalyst samples was investigated by HAADF-STEM (JEM-ARM-200F, JEOL). In the relevant experiments, the samples were dispersed in hexane and dropped on carbon paste mounted on the sample holder made of Si or Cu. The measurements were conducted using an accelerating voltage of 200 kV.

X-ray absorption fine structure (XAFS) measurements were performed on the AR-NW10A beamline of the Photon Factory Advanced Ring at the Institute of Materials Structure Science, High Energy Accelerator Research Organization, Tsukuba, Japan. A Si(311) double-crystal monochromator was used to obtain a monochromic X-ray beam, and spectra were obtained in the transmission mode. Pd(1 wt %)–ZrC and BN (dried at 300 °C) were mixed in an argon-filled glovebox, and the resulting mixture was pressed with a hand press apparatus to obtain a pellet, which was sealed in a plastic bag for the measurement to be performed. XAFS spectra were analyzed using Athena and Artemis software packages.³⁹ The FEFF6 code was used to calculate the theoretical spectra.⁴⁰

Pd metal was used for standards. The EXAFS data were analysed with the coordination numbers fixed as the ideal values. Bulk $ZrPd_3$ was also analysed to be compared with our Pd–ZrC catalyst in order to discuss the properties. The crystal structure of $ZrPd_3$ used in this study was reported by Norman and Harris.^{41,42} There are two specific sites for Pd in the structure, and the two sites were taken into account for EXAFS fitting procedures. In Table S1, Pd₁–M and Pd₂–M (M = Zr and Pd) denote the two specific sites of Pd in the structure. A Pd–C path was also considered for the Pd–ZrC sample.

Suzuki Coupling Reaction Conditions. All reactions were conducted in a 25 mL stainless-steel autoclave fitted with a glass mantel and a magnetic stirrer. In a typical reaction, 0.5 mmol organohalide, 0.8 mmol phenylboronic acid, 1.5 mmol K_2CO_3 , and 5 mg of Pd(1 wt %)–ZrC were mixed together in 5 mL of the solvent. The autoclave was then flushed three times with Ar, and the reactions were conducted in the autoclave at 25–60 °C. The products were analyzed by gas chromatography (GC), and product identification was further

confirmed by performing gas chromatography-mass spectrometry (GC-MS) measurements. The TOF was calculated from the reaction rate at a low conversion level and from the number of exposed Pd atoms estimated to be present on the catalyst surface *via* eqs 1 and 2

$$TOF = n_0 C / t n_{\text{catalyst}} \tag{1}$$

$$m_{\rm catalyst} = m_{\rm catalyst} N_{\rm Pd} / N_{\rm A} \tag{2}$$

where n_0 is the initial number of substrate moles, *C* is the conversion of the substrate at reaction time *t*, n_{catalyst} is the number of moles of Pd atoms exposed on the catalyst surface, m_{catalyst} is the weight of the catalyst, N_{Pd} is the amount of exposed Pd sites per gram of catalyst obtained when applying the CO pulse chemisorption method, and N_A is Avogadro's constant. For the recycling study, the Suzuki coupling reactions were performed with aryl halides and phenylboronic acid, maintaining the same reaction conditions as described above, except for the use of a recycled catalyst. After the completion of each reaction, the catalyst powder was washed with ethanol containing a certain amount of water several times to remove the organic and inorganic impurities from the used catalyst. Finally, the resultant powder was allowed to dry in vacuum at room temperature, weighed, and reused in the next run.

Nitroarene Hydrogenation Reaction Conditions. All reactions were conducted in a 25 mL stainless-steel autoclave fitted with a glass mantel, a 60 bar manometer, and a magnetic stirrer. In a typical reaction, 0.5 mmol substrates and 5 mg of the catalyst were mixed in 5 mL of the solvent. The autoclave was then flushed three times with H₂, pressurized with H₂ (0.5 MPa), and reactions were performed in the autoclave at room temperature (25 °C). The products were analyzed using GC with an external standard of *n*-hexadecane and the identity of the products was further confirmed from GC–MS measurements.

DFT Studies. All of the structural relaxation and electronic structure calculations were performed using DFT as implemented in the Vienna Ab initio Simulation Package (VASP).^{43,44} The generalized gradient approximation with the Perdew-Burke-Ernzerhof (PBE) functional⁴⁵ was adopted in the DFT calculations, and the core electrons were described using the projector augmented wave method.^{46,47} The ZrPd_a (0001) surfaces, based on the optimized bulk lattice parameters, were selected as the initial model because the (0001) surface of ZrPd₃ was calculated to be characterized by the lowest surface energy (1.27 Jm^{-2}) among the major faces, including the (0001), (11-20), and (1000) planes. The ZrPd₃ (0001) surfaces were modeled using a seven-layer slab with 2 × 2 lateral unit cells. A 20 Å-thick vacuum region was set to prevent interaction between the slabs. The central three layers of atoms of two surface models were kept fixed to hold the characteristics of realistic surfaces, and the rest of the unit cell was allowed to be fully relaxed during geometry optimization. A cut-off energy value of 500 eV and a Monkhorst-Pack Kmesh setting of $3 \times 3 \times 1$ were employed in the calculations for the ZrPd₃ (0001) surfaces. The vacuum level was defined as the energy level at which the electrostatic potential became constant. The atoms in the two bottom layers were then removed, and the five remaining layers were fixed and used for further molecule adsorption calculations. The surface of the ZrC-ZrPd₃ composite was modeled by placing a Zr₈Pd₂₄ cluster on three layers of ZrC (001) to confirm the electron donation effect of ZrC with a low value for the work function.

After the establishment of the surface structure, a bromobenzene molecule was placed on the $ZrPd_3$ (0001) plane, and the adsorption energy was screened by controlling adsorption points and angles. The data presented in this study were chosen on the basis of the state exhibiting the largest adsorption energy.

ASSOCIATED CONTENT

G Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.0c03416.

Detailed experimental HAADF-STEM, N₂ gas adsorption/desorption data, XRD data, and DFT results (PDF)

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Notes

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