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Construction of Pd/BiOCl Catalyst for Highly-selective Synthesis of Benzoin Ethyl Ether by Chlorine Promoted Coupling Reaction

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Keywords heterogeneous catalysis, coupling reaction, BiOCl , nucleophile , Pd nanoparticles, selectivity

Abstract Exploring novel catalyst supports with unique performance creates more opportunity for transforming organic chemicals in heterogeneous catalysis. In this paper, BiOCl is first presented as an effective support for Pd nanoparticles (NPs) toward application in the coupling reaction of benzaldehyde. The Cl^- ion dissociates from BiOCl, which forms nucleophile with Pd nanoparticles; this is key for the one-step synthesis of benzoin ethyl ether,

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the conversion and selectivity of which can reach to 100% and 97.9% at 100 °C, respectively. DFT calculations reveal that CI^- ions can be stabilized by stronger Bi–Cl bonds through doping of Fe ions in substituting Bi sites in BiOCl. The parallel catalytic evaluation using Pd/Fe-doped BiOCl catalyst shows the suppression of coupling reaction, conversely, demonstrating the crucial role of nucleophile. This work provides new insights into support tailoring for the synthesis of vital organic chemicals in heterogeneous catalysis by changing chemical reaction pathway.

1. Introduction

Benzoin ethyl ether is an effective and valuable photosensitizer, and has been widely used in printing and coating industries.¹⁻² As known, benzoin ethyl ether is produced industrially through the condensation of benzoin with ethanol in a certain way of homogeneous catalysis. During this process, cyanide or organics with strong nucleophilicity are usually used to synthesize benzoin, such as thiazolium salt, thiamine (vitamin B₁) or N-heterocyclic carbenes.³⁻⁶ However, not only cyanide is highly toxic, but organic catalysts used can lead to low conversion and by-products. Besides, the homogeneous synthesis cannot meet the challenges in reuse of catalysts and purification of products. Until recently, benzoin ethyl ether could be obtained in one-step by using Ni- or Zeolite-based heterogenous catalysts; it is a pity that the conversion is still not high enough.⁷⁻⁹ Therefore, the development of a heterogeneous catalyst continues to be a significant challenge for environment-friendly synthesis of benzoin ethyl ether with high conversion and selectivity through a cost-effective and one-step process.

Generally, the supported materials for catalysts not only play a role in the dispersion of metal sites to prevent their aggregation, but also influence catalytic activity and the reaction pathway through strong metal-support interactions.¹⁰⁻¹³ In this respect, various means have been performed to tailor the supports, including choosing varieties of supports, tuning the size

and morphology, and doping with some metal ions.¹⁴⁻¹⁹ Regarding halogen-based materials, BiOCl is gradually chosen as a model support in catalysis due to its well functionalization, low cost and environmental-friendly characteristic, while it is widely known as a photocatalyst.²⁰⁻²³ In particular, halogen elements are as active as CN^- for many well-known nucleophilic reactions owing to their strong polarity and electron-richness.²⁴⁻²⁷ Exactly, $CI^$ ions can dissociate from the BiOCl crystal structure because of the weak van der Waals forces.²⁸ Meanwhile, the volume and quality of halogen elements are larger than those of carbon elements, which makes the dipole moment and bond energy of C–X (X=halogen elements) greater than those of C–H. Therefore, the halogen elements drift away from C–X easily, which may facilitate the coupling of C–C bonds. On the other hand, owing to its typical light-responsive properties, the small size of noble metal catalysts can be loaded dispersedly on the BiOCl supports through a simple photo-reduction method.²⁹ Hence, the exploration of novel supports of BiOCl for noble metal catalysts may boost developments in the field of heterogeneous catalysis. To the best of our knowledge, such experimental phenomenon has not been reported yet.

Here, combining the methods of laser irradiation in liquids (LIL) and photoreduction, we report a new heterogeneous catalyst of Pd NPs supported on ultrathin BiOCl nanosheets. The catalytic performance of Pd/BiOCl catalyst is investigated, realizing the coupling reaction of benzaldehyde into one-step synthesis of benzoin ethyl ether, where the selectivity reaches to 97.9% with full conversion. The proposed mechanism is that the dissociated Cl⁻ ions form the nucleophile with Pd NPs promoting the coupling reaction of benzaldehyde. Based on DFT calculations, doping Fe ions in Bi sites is constructed to stabilize Cl⁻ ions in BiOCl structure through enhanced Bi–Cl bond energy. The parallel experimental results of Pd/Fe-doped BiOCl catalyst display the suppressing of coupling reaction along with another hydrogenation reaction, which demonstrates the decisive nucleophile role of dissociated Cl⁻ ions in coupling

reaction of benzaldehyde. This study may open up a new pathway of constructing supports for heterogenous catalysts in organic chemical transformations.

2. Results and discussion

2.1. Structural characterization of as-prepared catalysts

The supports of BiOCl and Fe-doped BiOCl were first synthesized by hydrothermal method and LIL technique. The LIL technique not only realizes the resizing of BiOCl structure but also dopes Fe elements into the BiOCl nanocrystalline structure in one-step. As shown in Figure S1, the as-prepared supports exhibit ultrathin nanosheet structure with a size of 50–200 nm. The X-ray diffraction (XRD) patterns (Figure S2) indicate that BiOCl and Fe-doped BiOCl samples all display the typical crystalline pattern of BiOCl. Subsequently, the Pd NPs were reduced to deposit on BiOCl and Fe-doped BiOCl through a photoreduction method.

To understand the structure of Pd NPs and distribution of Fe elements clearly, aberrationcorrected high-angle annular dark-field scanning TEM (AC HAADF-STEM) images and energy-dispersive X-ray (EDX) mappings of Pd/BiOCl and Pd/Fe-doped BiOCl were investigated. AC HAADF-STEM image (Figure 1a) reveals that Pd NPs are homogeneously dispersed onto BiOCl nanosheet. Figure 1b shows that the crystalline structure with an interplanar distance of 0.224 nm matches well with the (111) facet of Pd supported on the crystal structure of BiOCl. The corresponding EDX mappings (Figure 1c-d) further demonstrate the uniform distribution of Pd NPs on the supports. Similarly, Figure S3a shows the homogeneous distribution of Pd NPs on Fe-doped BiOCl nanosheet, displaying the same morphology characteristic with the catalyst of Pd/BiOCl. AC HAADF-HRSTEM image (Figure S3b) exhibits crystalline Pd loaded on Fe-doped BiOCl structure with an interplanar distance of 0.275 nm that matched well with (110) facet. Pd NPs and Fe elements were homogeneously distributed on Pd/Fe-doped BiOCl (Figure S3c). The corresponding XRD patterns displays no peaks of Pd NPs (Figure S4), which could be ascribed to the low amount

of Pd loading or the small size of Pd NPs. The Pd loading amount of Pd/BiOCl is 3.10 wt% estimated through inductively-coupled plasma atomic emission spectrometry (ICP-AES) analysis. For Pd/Fe-doped BiOCl, the amounts of Fe doping and Pd loading are 2.2 wt% and 2.95 wt%, respectively. To decode the effect of Cl⁻ ions with Pd NPs on catalytic performance, Pd/BiOCl catalysts with various amounts of Pd-loading and Fe-doping were also constructed using the same method (Table S1, Figure S5a-5d and S6a-6b). In addition, according to statistical analysis of 200 Pd NPs from TEM images, the average sizes of Pd NPs loaded on BiOCl-based support are in the range of 1.9–2.73 nm, indicating the size effect of Pd NPs on catalytic performance could be ignored (Figure S5e-5h and S6c-6d).

X-ray photoelectron spectroscopy (XPS) and X-ray absorption fine structure (XAFS) analyses were performed to determine the chemical state of the catalysts and the Fe doping position in the BiOCl structure. As shown in Figure 2a and Figure S7a, the Pd 3d XPS spectra of Pd/BiOCl and Pd/Fe-doped BiOCl both exhibit two chemical states of Pd, where a lower binding energy doublet was assigned to Pd⁰ with a Pd satellite peak and the higher was attributed to Pd^{2+} .^{30,31} The existence of Pd^{2+} species is ascribed to the adsorbate of $PdCl_4^{2-}$ on the surface of BiOCl-based Pd composites.³² Moreover, to analyze the Fe-doping types in the single-crystal structure of BiOCl, the 2.2 wt% Fe-doped BiOCl sample was further identified through XAFS. Figure 2b shows the Fe K-edge X-ray absorption near-edge structure (XANES) spectra of the Fe-doped BiOCl sample and other three reference materials, including Fe foil, FeO and Fe₂O₃. It can be seen that the energy position of Fe absorption edge for Fe-doped BiOCl is located at 7122.2 eV, very close to that of Fe₂O₃ (7122.3 eV), suggesting the main existence of Fe³⁺ in Fe-doped BiOCl, which is consistent with the XPS result (Figure S7b). Moreover, seen from the $k^{3}\chi$ (k) oscillation curves shown in Figure 2c, the peak shape and oscillation frequency of Fe K-edge for Fe-doped BiOCl is similar to that of corresponding Bi L-edge and quite different from that of Fe K-edge of Fe₂O₃, indicating the partial substitution of Bi site by doping Fe within Fe-doped BiOCl. The oscillation curves

of Fe K-edge for Fe-doped BiOCl shows a little positive shift relative to that of Bi L-edge over 4-9 Å⁻¹, which is owing to the atomic size difference between Fe and Bi atoms. Furthermore, the FT curves of Fe K-edge EXAFS for Fe-doped BiOCl shows two main peaks located at 1.56 and 2.7 Å, respectively, which was found to be similar with that of Bi L-edge and much different from that of Fe₂O₃ (Figure 2d). These results evidently confirm the replacing Bi site by doping Fe within Fe-doped BiOCl structure.

2.2. Catalytic performance of the catalysts

It is well-known that Pd-based catalysts for organocatalysis, especially Pd-catalyzed coupling reactions have become an active area of research and application.³³⁻³⁷ Herein, the coupling reaction of benzaldehyde was chosen to evaluate the catalytic performance of Pd/BiOCl catalyst for obtaining benzoin ethyl ether. The conversion efficiency and stability are displayed in Figure 3. The Pd/BiOCl catalyst with 3.10 wt% of Pd for the coupling reaction was investigated at different temperature (Figure 3a). At the reaction temperature within 100 °C, the conversion of benzaldehyde gradually increases and the selectivity to benzoin ethyl ether is more than 96%. At the temperature of 100 $\,$ °C, the conversion is 100% and the selectivity to benzoin ethyl ether reaches to 97.9%. As the temperature rises to 120 $^{\circ}$ C, the selectivity to benzoin ethyl ether slightly decreases to 95% with the conversion of 100%, indicating that the Pd/BiOCl catalyst retains excellent catalytic performance in a wide range of temperature. The Pd/BiOCl catalysts with different Pd loadings were also used to catalyze benzaldehyde (Figure 3b). Although the BiOCl support without Pd NPs has no catalytic ability, the 1.04, 2.08, and 3.10 wt% Pd/BiOCl achieve 59.9%, 92.3%, and 100% conversion of benzaldehyde with the similarly high selectivity to benzoin ethyl ether, respectively. With the Pd loading amount increasing to 4.0 wt%, the Pd/BiOCl still maintain high selectivity with full conversion. These results reveal that the combination of BiOCl with certain amount of Pd NPs can improve the conversion and facilitate high selectivity for transforming

benzaldehyde to benzoin ethyl ether. With the excellent performance, the stability of 3.10 wt% Pd/BiOCl was examined. As shown in Figure 3c, the 3.10 wt% Pd/BiOCl can maintain the conversion and selectivity to benzoin ethyl ether within 4 cycles after 3 h at 100 °C, reflecting the good stability in the coupling reaction. After 4 cycle tests, Pd NPs exhibit the aggregation and the mean size of 4.37 nm, larger than Pd nanoparticles before catalytic reactions (Figure S8). Meanwhile, the ICP-AES result displays that Pd loading amount is 2.57 wt%, showing slight metal leaching in this reaction system. However, the aggregation and metal leaching of Pd NPs has not affected greatly the catalytic performance of Pd/BiOCl in the coupling reaction.

Usually, the common supports loaded with Pd catalysts tend to realize the hydrogenation of benzaldehyde to benzyl alcohol under H₂ atmosphere, but the coupling reaction to benzoin ethyl ether would not occur. ^{38, 39} To verify the superiority of BiOCl support for Pd NPs in synthesizing benzoin ethyl ether, Pd/TiO₂, Pd/g-C₃N₄, and commercial Pd/C catalyst were used for catalyzing benzaldehyde. Pd/TiO₂ and Pd/g-C₃N₄ catalysts were also prepared through the same photoreduction method (Figure S9 and S10). These Pd-based catalysts were evaluated under the same conditions. As shown in Table 1, even though these Pd-based catalysts all show more than 95% conversion of benzaldehyde, but the high selectivity is toward to benzyl alcohol. That is to say, benzoin ethyl ether is not conducive to obtain by these Pd-based catalysts without Cl⁻ions. As discussed above, the support BiOCl loaded with Pd NPs can successfully achieve the production of benzoin ethyl ether with the exceptionally high conversion of 100% and selectivity of 97.9%. The Pd/bulk BiOCl also promote the coupling reaction of benzaldehyde, showing the conversion of 95.4% and selectivity of 85.3% toward benzoin ethyl ether. Ultrathin BiOCl nanosheets as support exhibit better catalytic activity than that of bulk BiOCl owing to its larger surface area for adsorbing reactants. The BiOCl-based Pd catalysts facilitate the coupling reaction, which was observed for the first

time. The supposed mechanism of the coupling reaction to benzoin ethyl ether is shown detailedly in Figure S11. Most important, CI^- ion escapes from BiOCl structure and becomes the dissociated CI^- ions under certain temperature and atmosphere pressure conditions. Given the existence of Pd NPs, the dissociated CI^- ions are considered to play the nucleophile role and facilitate the coupling of C–C bond originated from two benzaldehyde molecules. Then, benzoin forms and condenses with the ethanol solvent, favoring benzoin ethyl ether. These results show that the Pd/BiOCl catalyst is highly efficient for the coupling reaction of benzaldehyde to synthesize benzoin ethyl ether under the nucleophile role of the dissociated CI^- ions with Pd NPs.

2.3. The role of Cl⁻ in BiOCl with Pd

To clearly understand the effect of Cl⁻ ions dissociated from BiOCl structure, we performed DFT calculations to get in-depth knowledge of chemical bonds in BiOCl structure. It is found that doping Fe atoms into Bi atom sites in BiOCl can change the bond length of molecule, thus influencing the stability of whole structure. Figure 4 displays the structures of BiOCl and Fe-doped BiOCl. According to the theoretical calculation, the Bi₁–Cl₂ (or Bi₂–Cl₁) bond length of pure BiOCl is 3.12 Å and that of Fe-doped BiOCl is 2.97 Å. The Bi₁–Cl₂ (or Bi₂–Cl₁) bond length is shorter by 0.15 Å by doping Fe atoms in Bi atom sites, which leads to the increasement of Bi–Cl bond energy, i.e., the introduction of Fe atoms makes the Bi–Cl bond stronger, constraining Cl⁻ ions in the crystal structure. In view of this result, Fe-doped BiOCl supports are designed for Pd catalysts to stabilize Cl⁻ ions in BiOCl structure and decrease the escape of Cl⁻ ions from BiOCl.

The Pd/Fe-doped BiOCl catalysts with 0, 0.7, 2.2 wt% of Fe doping toward catalytic experiments were carried out. Based on the experimental results at 100 $^{\circ}$ C (Figure S12), the reaction temperature was optimized at 120 $^{\circ}$ C. As shown in Figure 5, the three catalysts all

show the conversion of 100%. Pd/BiOCl catalyst without Fe doing displays the selectivity of 95% for benzoin ethyl ether and 5% for benzyl alcohol at 120 °C. When 0.7 wt% Fe is doped into the crystal structure of BiOCl, the selectivity of benzoin ethyl ether drops to 84.1%, while the selectivity of benzyl alcohol increased to 15.9%. Subsequently, when the doping amount of Fe increases to 2.2 wt%, the selectivity of benzyl alcohol reaches to 99.5% as expected, indicating the hydrogenation of benzaldehyde becomes the dominant reaction. It obviously reflects that the coupling reaction is suppressed by doping Fe atoms to constrain Cl⁻ ions in BiOCl structure. These results demonstrate that dissociated Cl⁻ ions with Pd NPs have the decisive nucleophile action for the formation of C–C bond of two benzaldehyde molecules in the coupling reaction. Significantly, the support design for Pd catalyst can be controlled to determine whether Cl⁻ ions take effect in catalytic reaction.

3. Conclusion

In summary, we develop a tunable BiOCl-supported Pd catalyst for the coupling reaction of benzaldehyde. Pd/BiOCl catalyst successfully realizes synthesizing benzoin ethyl ether with superior conversion of 100% and selectivity of 97.9%. It is ascribed to that Cl⁻ ions dissociated from BiOCl exhibit the nucleophile role with Pd NPs on the formation of C–C bond in the coupling reaction of benzaldehyde. The dissociation of Cl⁻ ions can be controlled through enhancing Bi–Cl bond by doping Fe ions on the basis of DFT calculations. When Cl⁻ ions is not involved in coupling reaction, Pd/Fe-doped BiOCl catalyst is designed and facilitates hydrogenation property, which conversely demonstrate the key role of Cl⁻ ions in the coupling reaction. This work brings a new insight into the support construction of heterogeneous catalysts for expanding promising chemical synthesis and catalytic applications.

4. Experimental Section

Materials: Bismuth nitrate pentahydrate (Bi(NO₃)₃•5H₂O), potassium chloride (KCl), urea, thiourea, benzaldehyde, ethanol and Na₂PdCl₄ were purchased from Sinopharm Chemical

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Reagent Co. Ltd., PR China. Titanium oxide (TiO₂), iron chloride hexahydrate (FeCl₃•6H₂O), Pd/C (10%) were purchased from Aladdin Chemical Reagent Co. Ltd., PR China. Deionized water (18.2 M Ω) was employed in the all experiments. All chemicals were used without further purification.

Preparation of the support BiOCI: Firstly, a bulk BiOCI crystal was prepared as precursor by a hydrothermal method. 0.97014 g of Bi(NO₃)₃•5H₂O and 0.1491g of KCI were added into a Teflon-lined stainless autoclave with 30 mL deionized water. After the mixture was stirred for 30 min, the autoclave was heated at 160 \degree for 24 h. Then the bulk BiOCI material was collected and washed with deionized water and ethanol. The support BiOCI was prepared via the method of laser irradiation in water. Typically, 25 mg bulk BiOCI in 10 mL deionized water was irradiated by an unfocused laser with 355 nm in wavelength, frequency of 20 Hz, and an energy of 35 mJ per pulse under continuous stirring for 20 min. The resulting precipitates were collected and dried without washing, and the support BiOCI was obtained.

Preparation of Fe-doped BiOCI: In a typical preparation, $Fe_2O_3/BiOCI$ was synthesized as precursors by hydrothermal treatment of bulk BiOCI (75 mg) and FeCl₃•6H₂O (27mg) in a Teflon-lined stainless autoclave with 30 mL deionized water at 180 °C for 12 h. The obtained powder was washed and collected in reserve. And Fe-doped BiOCI was prepared by laser irradiating 25mg of Fe₂O₃/BiOCI in 10 mL deionized water. The laser parameters is the same with that of the preparation of the support BiOCI. Then, the 2.2 wt% Fe-doped BiOCI was obtained. Also, the doping concentration of Fe ions was controlled by different concentration of FeCl₃•6H₂O solution. When 10mg of FeCl₃•6H₂O was added into the autoclave for preparation of Fe₂O₃/BiOCI, the 0.7 wt% Fe-doped BiOCI was prepared by the laser irradiation in water with other conditions unchanged.

Preparation of Pd/BiOCl: A photoreduction method was used to load Pd NPs onto the support BiOCl. Typically, 20 mg of the support BiOCl were added into four quartz tubes with 30 mL deionized water. Then 0.3 mL, 0.6 mL, 0.8 mL, and 1.2 mL 13.6 mM of Na₂PdCl₄

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solution were added into the quartz tubes, respectively. The mixed solution was ultrasounded for 20 min. Finally, the quartz tubes were transferred to a photocatalyst reaction setup, where the solutions were illuminated under 500 W Xe lamp with 420 nm cutoff filters for 60 min. The obtained powders were washed with deionized water and ethanol for four times. Then 1.04 wt%, 2.08 wt%, 3.10 wt%, and 4.0 wt% Pd/BiOCl were synthesized and collected for future use. Moreover, the above-mentioned bulk BiOCl was chosen as support, and 3.46 wt% Pd/bulk BiOCl was synthesized in the same condition as that of Pd/BiOCl when adding 0.8 mL 13.6 mM of Na₂PdCl₄ Na₂PdCl₄ solution.

Preparation of Pd/Fe-doped BiOCl: In a typical synthesis, the preparation method is the same with that of Pd/BiOCl. 0.8 mL 13.6 mM Na₂PdCl₄ solution was added into a quartz tube containing 30 mL deionized water with 20 mg of Fe-doped BiOCl. Then the quartz tube was ultrasounded for 20 mins and illuminated under 500 W Xe lamp with 420 nm cutoff filters for 60 min. The obtained powder washed and collected was 2.95 wt% Pd/Fe-doped BiOCl.

Preparation of Pd/g-C₃N₄: In a typical preparation of catalyst Pd/g-C₃N₄, g-C₃N₄ was prepared by calcining the mixture of urea and thiourea at 550 °C for 2 h in air atmosphere. 20 mg of g-C₃N₄ and 0.8 mL 13.6 mM Na₂PdCl₄ solution were added into the 30 mL deionized water in a quartz tube. The mixture was ultrasounded for 20 min at room temperature and the catalyst was uniformly dispersed in the solution. Subsequently, the quartz tube was transferred to a photocatalyst reaction setup. The solution was illuminated under 500 W Xe lamp with 420 nm cutoff filters for 60 min. The final product was washed and collected with 1.05 wt% Pd loading by ICP-AES analysis.

*Preparation of Pd/TiO*₂: Pd/TiO₂ was prepared followed as: 0.8 mL 13.6 mM Na₂PdCl₄ solution was added into a quartz tube containing 30 mL deionized water with 20 mg of TiO₂. Then the solution was illuminated under 500 W Xe lamp for 60 min. The product was washed with deionized water and ethanol for four times. 3.97 wt% Pd/TiO₂ was successfully synthesized.

Characterization: A transmission electron microscope (FEI Tecnai G2 F20) with a 200 kV acceleration voltages was used to obtain the structural information of the products. X-ray diffraction (XRD) phase analysis of the prepared products was carried out using a Philips X'Pert system with Cu K α radiation ($\lambda = 1.5419$ Å; scanning rate, 1.0°/min). High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were obtained on a spherical aberration corrected transmission electron microscope (JEM-ARM 200F). And energy-dispersive X-ray spectroscopy (EDX) elemental mapping images were captured on high resolution TEM (Talos F200X). An X-ray photoelectron spectroscopy (XPS) system (Thermo ESCALAB 250) was used to analyze the valence states of the as-prepared samples. The binding energy was calibrated against C 1s (284.6 eV). Inductively coupled plasma atomic emission spectrometer (ICP-AES Optima 7300 DV) was used to estimate the Pd loading amount and Fe doping amount. X-ray absorption fine structure spectroscopy measurements were used to analyze the Fe doping location in the BiOCl crystal and performed at BL14W1 station in Shanghai Synchrotron Radiation Facility (SSRF). The electron storage ring of SSRF was operated at 3.5 GeV with a maximum current of 250 mA. The Bi L-edge spectrum was recorded in the transmission mode and the Fe K-edge spectrum was recorded in the fluorescence mode in ambient conditions.

Catalytic tests: In a typically catalytic reaction of benzaldehyde, 0.5 mmol of benzaldehyde, 15 mg of catalyst, and 5 mL of ethanol were added into a 25 mL stainless steel autoclave. The reaction solutions were under a magnetic stirrer with a speed of ~ 1000 rpm. N₂ at 1 MPa was used to purge the sealed autoclave three times and then H₂ with the pressure of 1 MPa was injected into the autoclave during the catalytic process. The gas pressure is controlled by a pressure gauge. An automatic temperature control apparatus controls the reaction temperature. When the temperature was set at a specific value, the reaction proceeded for a certain time. After the autoclave was cooled down, the autoclave contents were centrifuged to separate the catalyst and liquid product.

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Gas chromatography–mass spectrometry (GC-MS, Thermo Fisher Scientific-TXQ Quntum XLS) was used to identify the liquid product. The quantitative analysis of product was obtained by GC (Shimadzu, GC-2010 Plus), equipped with FID and a KB-WAX capillary column (Kromat Corporation, USA).

For the catalyst stability test, after every catalytic reaction, the catalyst was recycled by centrifuging the reaction content. Then the catalyst was washed with water and ethanol to remove the product and unreacted benzaldehyde. Finally the catalyst was dried under vacuum oven at 60 °C for the next test.

Calculation details: The spin-polarized DFT calculations are performed based on the generalized gradient approximation (GGA), as implemented in the Vienna Ab initio Simulation Package (VASP) 5.4.1 code.⁴⁰ The all-electron plane-wave basis set within the projector augmented wave (PAW) method is adopted and the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional is selected.⁴¹ The cutoff energy for expansion of the wave function into plane waves is set to be 500 eV. A dense enough k points sampling in the first Brillouin zone is examined with energy tolerance in 1 meV/atom. For geometric optimization, both lattice constants and atomic positions are relaxed until the forces on atoms are less than 0.01 eV/ Å and the total-energy change is less than 1 × 10⁻⁵ eV. The van der Waals interaction are considered through the cooperation of opt88-vdW functional.⁴²

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Figures and Tables



Figure 1. The structure and element distributions of Pd/BiOCl. (a) AC HAADF-STEM image.(b) AC HAADF-HRSTEM image. (c) and (d) AC HAADF-STEM images and corresponding EDX element mappings showing the distributions of Bi, Cl, O, and Pd.



Figure 2. (a) Pd 3d XPS spectrum of Pd/BiOCl. (b) Fe K-edge XANES spectra of Fe-doped BiOCl, Fe foil, FeO and Fe₂O₃. (c) Fe K-edge $k^3\chi$ (k) oscillation curves of Fe-doped BiOCl and Fe₂O₃, and Bi L-edge $k^3\chi$ (k) oscillation curves of Fe-doped BiOCl. (d) Fourier transform (FT) curves of Fe K-edge EXAFS spectra for Fe-doped BiOCl and Fe₂O₃ and of Bi L-edge EXAFS spectra for Fe-doped BiOCl.



Figure 3. (a) Conversion and selectivity of 3.10 wt% Pd/BiOCl catalyst for coupling reaction of benzaldehyde at different temperature after 5 h. (b) Activity and selectivity for coupling reaction of benzaldehyde with various Pd loadings of Pd/BiOCl after 5 h at 100 °C. (c) The stability test of 3.10 wt% Pd/BiOCl catalyst for coupling reaction of benzaldehyde after 3 h at 100 °C. (Reaction condition: 1 MPa H₂)

Table 1. Conversion and selectivity of Pd catalysts on different supports after 5 h of reaction at 100 $\,^{\circ}$ C and 1 MPa H₂.

benzaldehyde		pathway 1: hydrogenation Pd-based catalysts pathway 2: coupling reaction Pd/BiOCI catalyst		tion benz	benzyl alcohol	
	Catalysts	Pd (wt%)	Conversion (%)	Selectivity (%)		
				Benzoin ethyl ether	Benzyl alcohol	
	Pd/BiOCI	3.10	100	97.9	2.1	
	Pd/bulk BiOCl	3.46	95.4	85.3	14.7	
	Pd/TiO ₂	3.97	100	0	90.6	
	Pd/g-C₃N₄	1.05	95.1	0	91.5	
	Pd/C	10	100	0	47.5	



Figure 4. Structures and Bi–Cl bond lengths of BiOCl and Fe-doped BiOCl.



Figure 5. Conversion and selectivity toward benzaldehyde on the Pd/Fe-doped BiOCl with different Fe doping amounts (Pd: 2.95 wt%) after 5 h of reaction at 120 $^{\circ}$ C and 1 MPa H₂.