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Article

Photocatalytic C–X borylation of aryl halides by hierarchical SiC nanowire-supported Pd nanoparticles

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ARTICLE INFO

Article history:

Received 17 May 2019

Accepted 10 July 2019

Published 5 February 2020

Keywords:

Boronate esters

Carbon-halogen activation

Hierarchical SiC nanowires

Pd nanoparticles

Photocatalysis

ABSTRACT

Hierarchical SiC nanowire-supported Pd nanoparticles showed high photocatalytic activity for the C–X (X = Br, I) borylation of aryl halides at 30 °C. The SiC/Pd Mott-Schottky contact enhances the rapid transfer of the photogenerated electrons from SiC to the Pd nanoparticles. As a result, the concentrated energetic electrons in the Pd nanoparticles can facilitate the cleavage of C–I or C–Br bonds, which normally requires high-temperature thermal processes. We show that the present Pd/SiC photocatalyst is capable of catalyzing the transformation of a large variety of aryl halides to their corresponding boronate esters under visible light irradiation, with excellent yields.

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1. Introduction

Arylboronic esters are important synthetic intermediates, which can be converted to multiple functional groups and further employed to prepare a wide range of fluorinated organic compounds [1–6]. Traditionally, the synthesis of arylboronic esters is based on the reaction of aryl Grignard or lithium reagents with boron electrophiles [7–10]. Direct C–H borylation of arenes over precious metals such as Rh, Re, Ru, and Ir has recently emerged as a powerful tool for the synthesis of arylboronic esters, due to their efficiency and functional group compatibility [2–5,11–14]. In addition, highly selective transition metal-catalyzed borylation reactions of aryl halides, based on Pd, Fe, Co, Ni, Cu, Zn or even metal-free, have also been de-

veloped [15–27]. For example, Marder et al. [27] developed the Zn-catalyzed 1,2-selective dual C–H/C–X borylation of aryl halides. Recently, they also reported an efficient catalytic procedure for the selective C–F borylation of polyfluoroaromatic compounds using the *N*-heterocyclic carbene (NHC) Ni(0) complex as a catalyst and bis(pinacolato)diboron (B₂pin₂) as the boron source [23]. Geetharani et al. [20] also achieved borylation of aryl halides including aryl chlorides based on a Co(II)-NHC precursor, affording aryl boronates in good yields. Jiao et al. [28] reported the pyridine-catalyzed transition metal-free radical borylation of aryl halides. Photocatalysis has recently become particularly attractive in organic synthesis [29–34]. Significant recent progress has also been made in homogeneous photolysis-induced borylation. For example, Lari-

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This work was supported by the National Natural Science Foundation of China (21473232, 21673271, U1710112).

DOI: S1872-2067(19)63449-2 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 41, No. 2, February 2020

onov et al. [35–37] showed that aryl halides can be photochemically borylated under UV irradiation. Photoredox catalysts such as eosin Y or *fac*-[Ir(ppy)₃] (ppy = phenylpyridine) can also achieve the borylation of aryl diazonium salts or aryl halides in the same manner, under visible light [38–40]. Glorius et al. [41] even developed the decarboxylative borylation of aryl *N*-hydroxyphthalimide esters with visible light in metal-free conditions. Very recently, Guo et al. [42] reported a highly selective and general photocatalytic C–F borylation protocol that employs a rhodium biphenyl complex as triplet sensitizer and the Ni(0)-NHC catalyst for the C–F bond activation and defluoroborylation through a triplet energy transfer process.

Although homogeneous catalysts show high activity and selectivity, heterogeneous systems have also attracted attention due to their easy recycling. Zhu et al. [43] achieved (aryl) C–H activation and borylation using Ir(0) nanoparticles stabilized with the trihexyltetradecylphosphonium methylsulfonate ionic liquid as catalyst, in the presence of tetra-2-pyridinylpyrazine. Wang et al. [44] reported the Fe₂O₃ nanoparticle-catalyzed borylation of arenes with *tert*-butyl peroxide as oxidant, affording the corresponding aromatic boronic esters in moderate yields and with selectivity controlled by the electronic effects of the substituents. Pucheault et al. [45] found that highly active Pd nanocrystals coated with 1,10-bis(diphenylphosphino)ferrocene or tricyclohexylphosphane exhibited promising activity in the borylation of aryl bromides, with moderate to high yields at 100 °C. Liu et al. [46] synthesized a molecular heterogeneous catalyst based on Ir by metalation of one-dimensional organosilica nanotubes containing 2,2'-bipyridine ligands with an Ir complex; the catalyst showed high activity and durability in the C–H borylation of arenes because of the effective suppression of Ir-bpy complex aggregation and fast transport in the short nanotubes. Lin et al. [47] synthesized a terpyridine-based metal-organic layer (TPY-MOL) and metalated it with CoCl₂ to obtain a Co^{II}-TPY-MOL catalysts for benzylic C–H borylation. They claimed that the formation of the MOL-stabilized Co^{II}-(TPY)²⁻ species endowed the catalyst with unique and enhanced catalytic activities for C–H borylation.

To obtain a satisfactory product yield, most heterogeneous borylation processes are still conducted at elevated temperatures and with ligand additives. Because improving the catalytic efficiency by increasing the temperature is an energy-intensive process, enhancing the activity of a solid catalyst at lower temperatures by sunlight irradiation would represent a significant breakthrough. Moreover, electron-rich active sites in catalysts can accelerate the activation of C–halogen bonds; hence, there is considerable interest in employing light irradiation as an alternative approach to increase the electron density at active sites and promote the reactions involving aryl halides. Recently, Chandrashekar et al. [48] reported the photocatalytic transformation of diazonium salts to arylboronates with high turnover number in the presence of water-soluble 3-mercaptopropionic acid (MPA)-capped, CdSe-based quantum dots. The CdSe dots transfer excited-state electrons to the substrate to form aryl radicals, which react with the borylating

agent to form the arylboronate. Our group previously employed a photoresponsive cubic β -SiC semiconductor with a band gap of 2.4 eV to absorb light and generate energetic electrons [49]. The transfer of these electrons to Pd can greatly enhance its activity in the photocatalytic Suzuki-Miyaura coupling [50], Sonogashira [51], Heck [52], and nitroarene hydrogenation [53] reactions. Herein, we report a catalyst consisting of Pd nanoparticles supported on β -SiC nanowires with hierarchical structure (Pd/SiC), designed for the photocatalytic borylation of aryl iodides and aryl bromides with B₂pin₂. The catalyst exhibits excellent activity under visible light irradiation at 30 °C.

2. Experimental

2.1. Preparation of Pd/SiC

Hierarchical SiC nanowires were prepared by a sol-gel process followed by carbothermal reduction [54,55]. The Pd/SiC catalyst was prepared by a one-step impregnation-reduction method. Briefly, a 485 mg amount of SiC nanowires was dispersed in 14.1 mL of an aqueous solution of Pd(NO₃)₂ (0.01 M). After 30 min of stirring, 10 mL of an aqueous solution of lysine (0.53 M) was added dropwise to the above mixture. After another 30 min of stirring, 5 mL of an aqueous NaBH₄ solution (0.35 M) was added dropwise, and 5 mL of 0.3 M HCl was then added to the above suspension. Finally, the mixture was left in air for 24 h. The solid product was then separated, washed, and dried to obtain the Pd/SiC catalyst with a metal loading of 3 wt%. According to inductively coupled plasma mass spectrometry (ICP-MS, Perkin-Elmer ELAN 5000) measurements, the actual Pd content was 2.87 wt%. Pd/TiO₂, Pd/Al₂O₃, and Pd/SiO₂ catalysts with the same Pd loading, as well as Pd/SiC catalysts with different Pd loadings, were also prepared by the same method but with different supports or different amounts of Pd(NO₃)₂.

2.2. Characterization

The microstructures of the catalysts were investigated by high-resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy (STEM). X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos XSAM800 spectrometer, using an Al K α ($h\nu$ = 1486.6 eV) X-ray excitation source. The crystalline phases were characterized by X-ray diffraction (XRD, Rigaku D-Max/RB). Diffuse reflectance UV-Vis absorption spectra were measured with Al₂O₃ as the reference, using a UV-3600 spectrophotometer (Shimadzu). Photoluminescence (PL) spectra were recorded using a Hitachi F-4500 fluorescence spectrophotometer. We ensured that the quality and tablet thickness of the different samples used in the UV-Vis absorption and PL measurements were consistent.

2.3. General procedure for photocatalytic reactions

Unless specified otherwise, all reactions were conducted in

ambient Ar atmosphere at 30 °C. A mixture of aryl halides (1 mmol), B₂pin₂ (1.2 mmol, 305 mg), base (1 mmol, 98 mg), and Pd/SiC catalyst (40 mg) was suspended in 10 mL of *N,N*-dimethylformamide (DMF) in an oven-dried 25 mL quartz vial equipped with a magnetic stirring bar. During the reaction, the mixture was stirred at 500 rpm using a magnetic stirrer and then exposed to a xenon lamp with a wavelength range of 375 to 800 nm (the spectral output is shown in Fig. S1). A low-pass optical filter was employed to block wavelengths below 400 nm. The light intensity was maintained at 0.65 W/cm². The effect of the light wavelength on the catalytic performance was investigated using various light-emitting diode (LED) lamps with different wavelengths.

After reaction, the mixture was diluted with dichloromethane (DCM, 10 mL). The organic phase was extracted and filtered through a millipore filter (pore size: 0.22 μm). Then, 0.5 mmol of *n*-dodecane was added as an internal standard. The product yield was determined by gas chromatography-mass spectrometry (GC-MS, Bruker Scion SQ 456) using *n*-dodecane as the internal calibration standard. The reported values are the average of two experiments. The yields were calculated based on the amount of aryl halide. The residue was purified by column chromatography on silica gel (200–300 mesh; eluant: hexane/ethyl acetate) to isolate the desired product.

All NMR spectra were recorded at ambient temperature using a Bruker Avance III 400 (¹H, 400 MHz; ¹³C{¹H}, 101 MHz; ¹⁹F, 376 MHz). The reported ¹H NMR chemical shifts are relative to tetramethylsilane (TMS) and referenced via the residual proton resonances of the corresponding deuterated solvent (CDCl₃: 7.26 δ). The reported ¹³C{¹H} NMR spectra are referenced to TMS via the carbon signals of the deuterated solvent (CDCl₃: 77.16 δ), whereas the quoted ¹⁹F NMR chemical shifts are relative to CFCl₃ as external standard. All ¹³C NMR spectra were broad-band ¹H decoupled. High-resolution mass spectrometry (HRMS) measurements were carried out on a Thermo Scientific Exactive Plus instrument equipped with an Orbitrap analyzer. Electrospray ionization (ESI) measurements were conducted using a heated ESI (HESI) source with an auxiliary gas temperature of 50 °C. Atmospheric pressure chemical ionization (APCI) measurements were conducted using an APCI source with a corona needle; the auxiliary gas temperature was 400 °C.

3. Results and discussion

Using iodobenzene **1a** (Table 1) as the substrate, we screened different bases, solvents, and Pd loading amounts in Pd/SiC to assess the scope and limitations of the present photocatalytic borylation reaction (see Tables S1–S3 in the Supporting Information for details). The borylated product **1b** (phenylpinacolborane) was obtained in the highest yield of 95% using potassium acetate (KOAc) as base and 3 wt% Pd/SiC as photocatalyst in DMF. Compared with those of other supported catalysts for heterogeneous borylation of aryl halides, reported in previous studies (Table S4), the photocatalytic performances of Pd/SiC exhibit some improvements both in reaction conditions and catalyst repeatability. The reaction did

Table 1

Substrate scope of Pd/SiC-photocatalyzed borylation of aryl halides under visible light irradiation.

(a: 1 equiv.)	(b)

95% (87%) [3h]

90% (81%) [3h]

86% (77%) [3h]

85% (78%) [3h]

90% (83%) [3h]

89% (81%) [3h]

82% (74%) [5h]

90% (82%) [5h]

86% (76%) [3h]

89% (75%) [8h]

66% (51%) [10h]

99% (92%) [6h]

84% (75%) [12h]

80% (69%) [12h]

89% (80%) [10h]

80% (73%) [12h]

70% (61%) [12h]

74% (68%) [12h]	

Reaction conditions: 1 mmol of aryl halide, 1.2 mmol of B₂pin₂, 1 mmol of KOAc, and 40 mg of Pd/SiC in 10 mL of DMF, in Ar at 30 °C under Xe lamp irradiation (0.65 W/cm²). Yields determined by GC-MS; isolated yields are shown in parentheses and reaction times in square brackets. Benzene and its derivatives from hydrodehalogenation reactions were the main byproducts.

not occur under light irradiation without any catalyst, and no product was detected using only pure SiC as catalyst. Control experiments showed that the **1b** yield decreased to 5% in the dark under identical conditions. Moreover, the **1b** yield decreased linearly when the light intensity was decreased while keeping all other experimental conditions unchanged (Fig. 1(A)), indicating that the reaction was driven by light irradiation. The reduced catalytic activity is likely due to the decrease in the number of activated electrons generated at low irradiation intensity. The obtained linear relationship indicates that the process should be first order in photon, suggesting that the reaction is dominated by a single photon absorption event. Fig. 1(B) shows the dependence of the catalytic activity on the irradiation wavelength, determined using procedures similar to those reported in literature [50–53]. The **1b** yields in irradiation wavelength ranges of 400–800, 450–800, 500–800, 550–800, and 600–800 nm were 95%, 61%, 39%, 23%, and 10%, respectively. As the yield of **1b** without light irradiation was only 5%, the light-induced yields within each wavelength range were about 34% (400–450 nm), 22% (450–500 nm), 16% (500–550 nm), 13% (550–600 nm), and 5% (600–800 nm). When the reaction was conducted under UV irradiation (200–300 nm, 0.3 W/cm²) with a light intensity of 0.3 W/cm², a

Fig. 1. Dependence of catalytic activity of 3 wt% Pd/SiC in the photocatalytic borylation of iodobenzene with B₂pin₂ on the intensity (A) and wavelength (B) of the irradiation. The red line in (B) is the absorption spectrum of the catalyst.

nearly 100% yield of **1b** was achieved. Usually, the higher energy associated with short-wavelength light results in the bound energy of Pd going to higher energy levels, facilitating chemical reactions on the Pd nanoparticles [56]. The above values are consistent with the UV-Vis absorption data of the Pd/SiC catalyst.

We further examined the aryl halide scope in the present photocatalytic borylation under optimized conditions, and the results are summarized in Table 1. Aryl iodides with electron-withdrawing (**2a–7a**) or electron-donating (**7a–11a**) substituents showed high to moderate reactivity. Besides the aryl iodides, aryl bromides (**12a–18a**) were also converted to their corresponding boronate esters over Pd/SiC under visible light irradiation. However, the present catalyst could not convert aryl chlorides to the target products.

Different microscopic and spectroscopic methods were used to characterize the structural features of the Pd/SiC catalyst. Hierarchical SiC nanowires (Fig. S2) were employed to support Pd nanoparticles, because the hierarchical structure promotes an increase in light absorption and specific surface area, as well as a reduction in the recombination rate of photoelectron and holes, thus improving the photocatalytic activity [57,58]. The transmission electron microscopy (TEM) images of Pd/SiC (Fig. 2(A) and S3) show that the Pd nanoparticles are uniformly dispersed on the support and have an average diameter of 3.7 nm (Fig. S4). Based on the HRTEM image in Fig. 2(B), the interplanar crystal spacing of the Pd nanoparticles is 0.23 nm, corresponding to the Pd (111) crystal faces. In the UV-Vis absorp-

tion spectra (Fig. 1(B) and S5(A)), the strong absorption peak at ca. 375 nm originates from SiC, while the absorption above 500 nm mainly derives from the near-infrared absorption of SiC and the reflection from the sample. However, Pd/SiC shows stronger absorption peaks than pure SiC in both the UV and visible ranges. Generally, the binding energy (BE) values of metallic Pd are in the ranges of 334.7–335.5 eV for Pd 3d_{5/2} and 340.3–340.8 eV for Pd 3d_{3/2}. Therefore, the Pd particles in Pd/SiC are metallic (Fig. 2(C)). However, the lower values of the Pd 3d BE (334.7 and 340.1 eV) in the Pd/SiC sample suggest an electron transfer to Pd. The work functions of SiC and Pd are 4.0 and 5.12 eV, respectively; when they are in contact with each other, a built-in potential is formed, which forces the electrons to transfer from SiC to Pd, resulting in electron enrichment of Pd [18].

5,5-Dimethyl-1-pyrroline *N*-oxide (DMPO) is an electron-trapping agent that can capture electrons from Pd nanoparticles [59]. When 0.5 mL of DMPO was added in the photocatalytic borylation of iodobenzene, the **1b** yield decreased to 6%. This yield is almost the same as that observed in the dark reaction, suggesting that the light-driven reaction is completely quenched. In addition, triethanolamine (TEA) was employed as a scavenger to trap the photogenerated holes on the surface of SiC. No product was detected when 0.8 mL of TEA was added to the reaction system. The above results indicate that the coupling reaction cannot proceed without the reduction of electrons or oxidation of holes.

Thus, a visible light photoinduced catalytic process could

Fig. 2. TEM image (A), HRTEM image (B), and XPS spectrum (C) of Pd/SiC.

contribute to the enhanced borylation of aryl halides over the Pd/SiC catalyst. When Pd nanoparticles are dispersed on the surface of SiC, they can form a Schottky junction. As the work function of SiC (4.0 eV) is lower than that of Pd (5.12 eV), a built-in potential of 1.12 eV can form between them. This potential forces electrons to transfer from SiC to Pd nanoparticles and results in electron-rich Pd nanoparticles. In the room-temperature PL spectra of pure SiC and Pd/SiC under excitation at 325 nm (Fig. S5(B)), the PL peaks of both samples range from 400 to 550 nm, in agreement with the literature. However, the PL intensity of Pd/SiC shows an obvious decrease compared with that of pure SiC, indicating that the recombination of the photogenerated electrons and holes has been effectively suppressed. This further confirms the transfer of electrons from SiC to the Pd particles. The electron transfer results in a positively charged region in SiC and negatively charged Pd nanoparticles. The C–X oxidative addition is often the rate-determining step in the catalytic cross-coupling reactions of aryl halides, while transmetalation is generally a facile process. The highly negatively charged Pd particles facilitate the carbon-halogen bond cleavage, and thus enhance the catalytic activity.

The performances of Pd/TiO₂, Pd/Al₂O₃, and Pd/SiO₂ with 3 wt% catalyst loading in the **1a** borylation were also studied. Without irradiation, the **1b** yield was 8% for Pd/TiO₂, 3% for Pd/Al₂O₃, and 5% for Pd/SiO₂, while under irradiation the yields increased to 24%, 15%, and 18%, respectively. The slightly increased activity of these catalysts under visible light is attributed to the Pd nanoparticles absorbing light through interband electronic transitions to produce photoexcited electrons, which can promote the breaking of C–I bonds. These results further confirm that the intrinsic catalytic activity of Pd is significantly enhanced by visible light irradiation when SiC is used as the support.

We also determined the thermodynamic parameters for the borylation of iodobenzene and bromobenzene with B₂pin₂ in the temperature range 30–100 °C, under irradiation and in the dark (Fig. 3). The apparent activation energy for the borylation of iodobenzene was calculated to be 47.3 kJ/mol under irradiation (400–800 nm) and 73.1 kJ/mol in the dark, based on the Arrhenius equation. Using bromobenzene as substrate, the apparent activation energies with and without irradiation were

59.8 and 92.9 kJ/mol, respectively. The large difference in activation energy suggests that the reaction mechanisms with and without light irradiation are very different. The light-activated process is mainly driven by charge carriers. The energetic electrons concentrated in the Pd particles activate the adsorbates to form excited states and move to a different potential energy surface to take part in the reaction. The process without light irradiation is mainly driven by phonon effects. The thermal energy results in the adsorbed reactants to move to the ground-state potential energy surface of the product.

The main advantages of a heterogeneous catalyst lie in its good stability, recyclability, and ease of separation. To investigate the recyclability of the Pd/SiC catalyst, the used catalyst was regenerated and tested for five cycles under the same reaction conditions, and did not show any measurable loss in catalytic activity (Fig. S6(A)), which indicates its excellent stability. The TEM images of the catalyst after five runs show no obvious change in the size and morphology of the Pd nanoparticles (Fig. S6(B)).

4. Conclusions

In summary, we have shown that Pd nanoparticles supported on hierarchical SiC nanowires can effectively utilize visible light to catalyze the C–X borylation of aryl halides to the corresponding boronate esters under mild conditions. The Mott-Schottky heterojunction between Pd and SiC can continuously transfer photogenerated electrons to the Pd nanoparticles. The highly negatively charged Pd can facilitate the cleavage of C–I or C–Br bonds, which is the rate-determining step in catalytic cross-coupling reactions of aryl halides. This work will inspire further applications of transition metal-decorated, semiconductor-supported metal nanoparticles as photocatalysts for a wide range of organic transformations driven by light.

Acknowledgments

We are grateful to the Alexander von Humboldt Foundation for providing a postdoctoral fellowship to X. N. G.

Fig. 3. Activation energy of iodobenzene (A) and bromobenzene (B) borylation with and without irradiation.

Graphical Abstract

Chin. J. Catal., 2020, 41: 357–363 doi: S1872-2067(19)63449-2

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Hierarchical SiC nanowire-supported Pd nanoparticles showed high photocatalytic activity for the C–X (X = Br, I) borylation of aryl halides at 30 °C, due to the rapid transfer of photogenerated electrons from SiC to Pd through their Mott-Schottky contact.

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具有分级结构的SiC纳米线负载的Pd纳米颗粒光催化芳基卤化物硼化反应

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摘要: 芳基硼酸酯作为一种重要的有机中间体, 在C–C, C–N和C–O键的构筑以及C–X键的转换中有着广泛的应用, 其传统合成方法主要是用格氏试剂或有机锂试剂, 但该方法的官能团耐受性较差, 且对反应环境敏感。在均相催化体系下, 过渡金属催化芳烃的C–H和C–X键硼化反应成为合成芳基硼酸酯化合物的重要途径, 虽然活性和选择性很高, 但催化剂难于分离, 且多数反应需要昂贵的配体, 限制了其在工业上的大规模应用。多相催化体系虽然解决了分离回收的问题, 但是催化效率大多较低。近年来, 由于光催化能够有效利用太阳能, 在温和条件下促使反应进行, 并且能够定向的选择性合成目标产物, 提高目标产物的产率, 因此其在有机合成中的应用引起了广泛的关注。

本文以具有分级结构且能够响应可见光的SiC纳米线为载体, 并通过液相还原法制备负载量为3 wt%的Pd/SiC催化剂。TEM照片可以看出, Pd纳米颗粒均地分散在SiC表面, 平均粒径为3.7 nm。UV-Vis图谱表明, SiC负载Pd以后可明显提高其对可见光的吸收。Pd/SiC在可见光(400–800 nm)照射下, 在30 °C和常压Ar氛围下即可实现碘苯脱碘硼化, 苯硼酸频哪醇酯的收率高达95%。Pd/SiC在可见光作用下, 对其它碘苯类和溴苯类化合物的光催化硼化均具有较好的普适性。在暗反应条件下, 苯硼酸频哪醇酯的收率仅为5%。并且, 转化率能够随着光强度的增强而增加。同时, 不同的波长范围对光反应的贡献率也不同, 400–450, 450–500, 500–550, 550–600和600–800 nm的光反应贡献率分别为34%, 22%, 16%, 13%和5%, 这与催化剂的紫外可见吸收光谱相一致, 充分说明反应主要为光驱动反应。Pd/SiC催化剂也具有较好的可重复使用性, 经过5次循环使用后, 催化活性依然保持在较高的水平。

光反应和暗反应活化能的显著差别, 说明二者的机理不同。理论研究发现, SiC的功函为4.0 eV, 低于Pd(5.12 eV), 当Pd负载在SiC表面时, 能够形成Mott-Schottky接触, 使SiC吸收可见光生成的光生电子能够迅速的传递到Pd活性位。XPS表征显示, Pd在Pd/SiC催化剂中以金属态Pd⁰的形式存在, 并向低结合能方向移动, 说明SiC中的电子向Pd迁移, 增加了Pd原子周围的电子云密度。同时, 光致发光光谱中, Pd/SiC位于400–550 nm的特征峰与SiC相比, 强度明显减弱, 说明光生电子和空穴的分离效率增强。据此我们推断, 光生电子迅速从SiC传递到Pd使Pd活性位表面富电子化, 进而快速活化和断裂芳基卤化物中的C–I或C–Br键, 有效提高催化活性。

关键词: 芳基硼酸酯; C–X键硼化; SiC; Pd纳米颗粒; 光催化

收稿日期: 2019-05-17. 接受日期: 2019-07-10. 出版日期: 2020-02-05.

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基金来源: 国家自然科学基金(21473232, 21673271, U1710112).

本文的电子版全文由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).