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Highly Active Palladium-Based Catalyst System for the Aerobic Oxidative Direct Coupling of Benzene to Biphenyl

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A highly efficient Pd-containing catalytic system for the intermolecular direct C–H homocoupling of benzene to biphenyl has been developed. The catalytic system was composed of $Pd(OAc)_2$ with trifluoromethanesulfonic acid (TfOH) as an additive and O_2 as the sole oxygen source in the absence of any metal-containing cocatalyst. An excellent efficiency of Pd^{II} with the acidic additive was attained in the aerobic oxidation of benzene to biphenyl. A high yield (25.3 %) and selectivity (98 %) were achieved by using a small amount of $Pd(OAc)_2$ (0.07 mol %) and TfOH, which gave a high turnover number (180) for Pd species. Theoretical calculation by DFT and UV/Vis absorption spectra illustrated that the formation of electropositive Pd^{II} species in the presence of TfOH contributed to the high efficiency of the catalytic system.

Introduction

Catalysts are used widely in industry, in which the utilization of noble metals is often involved because of their irreplaceable and efficient role in many reactions.[1,2] However, noble metals are hardly renewable resources; therefore, it is necessary to promote their efficiency, which can be achieved by replacing the noble metals with non-noble metals or by decreasing the dosage of noble metals.[3–7] As many organic transformations rely strongly on noble-metal catalysts,[8] it is desirable to promote the catalytic efficiency of the noble metals for these organic syntheses, which requires the fabrication of highly efficient catalytic systems towards target reactions.

The liquid-phase aerobic oxidative direct coupling of benzene to biphenyl is a promising atom-efficient and environmentally friendly way to produce biphenyl, an important intermediate in the synthesis of polymers and liquid crystals.[9–11] This reaction features a much lower temperature than the industrial vapor-phase dimerization of benzene.[12] It also avoids the formation of undesirable byproducts such as copper iodide or boric salts in the Ullmann reaction and Suzuki coupling,[13,14] although the latter two routes can produce biphenyl in high yields. The catalytic activation of the C–H bond in the robust substrate of benzene causes substantial barriers in the direct catalytic synthesis, thus the aerobic oxidative direct coupling of benzene to biphenyl normally relies on Pd-containing catalytic systems. In early studies, the reaction was initiated using a stoichiometric amount of Pd salt or under high oxygen pressures, which gave low biphenyl yields and turnover numbers (TON).[15–18] As a result, various metal-containing cocatalysts were adopted to promote the efficiency of the Pd catalyst.[19–26] $PdCl_2$ combined with $Zr^{IV}/Mn^{II}/Co^{II}$ species led to biphenyl in a high yield (~84 %) with a TON of ~12.[24] $Pd(OAc)_2$ combined with a 1:1 mixture of $H_4PMo_{11}V_1O_{40}$ and $H_3PMo_{12}O_{40}$ gave a high TON of 109 with a yield of 14.3 %.[25] The selectivity to biphenyl was 79 % because of the formation of byproducts: a mixture of *o*-, *m*-, and *p*-terphenyls along with a small amount of phenol. To enhance the solubility of oxygen in the reaction medium, CO_2-expanded solvent was applied in the $Pd(OAc)_2$-$Cu(OAc)_2$ catalytic system to give a biphenyl yield of 19 %.[26] Nevertheless, to date, the number of studies related to the direct coupling of benzene to biphenyl is still limited, and the efficiency of Pd catalyst for these biphenyl syntheses is unsatisfactory if we consider the yield, selectivity, and TON. Moreover, previous reactions were performed with the assistance of a stoichiometric amount of metal-containing cocatalyst, and yet no efficient system that involves metal-free additives has been reported for the Pd-catalyzed aerobic oxidative direct coupling of benzene to biphenyl.

Many efforts have been made to promote the catalytic efficiency of the Pd-catalyzed coupling of aryls by using ligands or acids.[27–30] Ligands such as pyridine cannot only hold back Pd aggregation by stabilizing Pd^0 species but also promote the activity of Pd species in the catalytic process. For example, Stahl et al.[31,32] found that 2-fluoropyridine used as a ligand can enable superior levels of chemo- and regioselectivity in the Pd-catalyzed aerobic oxidative coupling of *o*-xylene to 4,4′-bixylyl. Acids such as trifluoroacetic acid (TFA) could accelerate the electrophilic substitution between Pd ions with aryls by generating more electropositive $[Pd^{II}O_2CCF_3]^+$ species.[33] She et al.[34] realized the C–H olefination of (hetero)arenes at room temperature by using a highly electrophilic Pd species $[Pd(TFA)_2]$, which was generated in situ through the interaction of $Pd(OAc)_2$ with TFA. Houlden et al.[35] highlighted the activity of $Pd(OTs)_2$ in the Pd^{II}-catalyzed diene 1,2-carboamination reac-

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tion, which involved the in situ generation of a highly electrophilic Pd^{II} species Pd(OTs)$_2$ from Pd(OAc)$_2$ and *p*-toluenesulfonic acid (TsOH). Ma and Tian[36] developed a highly regioselective halogenation reaction for symmetrical and unsymmetrical aromatic compounds in the presence of palladium diacetate and TsOH, in which the actual catalytic species was Pd(OTs)$_2$. Xiao et al.[37] accomplished the *ortho* C–H amidation of aromatic ketones with both sulfonamides and amides by using an electron-deficient Pd complex, Pd(OTf)$_2$, and indicated that trifluoromethanesulfonic acid (TfOH) was useful to tune the electrophilicity of Pd^{II} to achieve the difficult C–H activation. Hitherto, no study appears to date in which these organic ligands or acids are used in the Pd-catalyzed aerobic oxidative direct coupling of benzene to biphenyl.

In this work, we construct an efficient Pd-related catalytic system, Pd(OAc)$_2$-TfOH, for the direct aerobic oxidative coupling of benzene to biphenyl with O$_2$ as the sole oxygen source in the absence of any metal-containing cocatalyst. Catalyst selection, the function of additives, solvent composition, catalyst amount, TfOH concentration, oxygen pressure, reaction time, and reaction temperature are examined systematically. TfOH is proved to be an effective additive for the coupling of benzene to give a high yield, selectivity, and TON towards biphenyl. To gain an insight into the catalytic process, theoretical calculations by DFT are performed to explore the charge distribution of various Pd salts. UV/Vis absorption spectra of Pd(OAc)$_2$ in aqueous acetic acid solution are collected to understand the state of Pd species in the presence of various acidic additives.

Results and Discussion

Screening of Pd-related catalysts and additives for the oxidative coupling of benzene

The direct oxidative coupling of benzene with O$_2$ proceeds with the use of Pd-containing catalytic systems in aqueous acetic acid solution. Reaction systems give the major coupling product biphenyl and a small amount of hydroxylation product phenol. No other byproduct is observed by GC. The catalytic performance is investigated by screening various Pd species and additives (Table 1 and Figures 1 and 2). The reaction occurs in a mixed solvent of HOAc/H$_2$O (3:2 by volume) at 105 °C for 7.5 h.

A trace amount of biphenyl (yield $<0.5\%$) is detected in the absence of any catalyst (Table 1, entry 1). Pd(OAc)$_2$ alone gives a yield to biphenyl of 5.8% with a TON of 40 (Table 1, entry 2), which is superior to the yields to biphenyl over other Pd salts such as PdCl$_2$ (3.2%), bis(acetonitrile)dichloropalladium(II) (PdCl(PhCN)$_2$, 2.2%), and bis(dibenzylideneacetone)palladium (Pd(dba)$_2$, 5.1%; Figure 1). By contrast, no product forms with the use of a commercial Pd/C catalyst (10 wt% Pd on carbon), which suggests that the Pd^{II} ion acts as the active site for the aerobic oxidative coupling of benzene.[38]

If Pd(OAc)$_2$ is used alone, the biphenyl yield is relatively low, and apparent palladium black precipitation is observed at the end of the reaction, which indicates the deactivation of the catalyst. As a result, various additives are used to improve the activity and accelerate the regeneration of the active Pd^{II} spe-

Table 1. Catalytic performance of different Pd-based catalytic systems in the aerobic oxidative coupling of benzene to biphenyl.[a]

Entry	Catalyst	Additive	Yield [%][b]	Selectivity [%][c]	TON[d]
1	none	none	0.5	–	–
2	Pd(OAc)$_2$	none	5.8	98.3	40
3	Pd(OAc)$_2$	TfOH	25.3	98.5	180
4	none	TfOH	0.5	–	–
5	Pd(OAc)$_2$	TsOH	23.8	98.1	170
6	Pd(OAc)$_2$	MSA	22.4	97.7	160
7	Pd(OAc)$_2$	TFA	19.8	98.4	141
8	Pd(OAc)$_2$	TFE	10.8	97.6	77
9	Pd(OAc)$_2$	BZA	2.3	97.8	15
10	Pd(OAc)$_2$	PTA	0.2	97.9	1
11	Pd(OAc)$_2$	NaOTf	3.1	97.5	22

[a] Reaction conditions: benzene (30 mmol), Pd(OAc)$_2$ (0.022 mmol, 0.07 mol%), additive (1.67 mmol), acetic acid (6 mL), H$_2$O (4 mL), O$_2$ (3 atm), 105 °C, 7.5 h. [b] Biphenyl yield [%] = 2 × mmol biphenyl/mmol initial benzene. [c] Biphenyl selectivity [%] = 2 × mmol biphenyl/(2 × mmol biphenyl + mmol phenol). [d] Turnover number = mmol biphenyl/mmol catalyst.

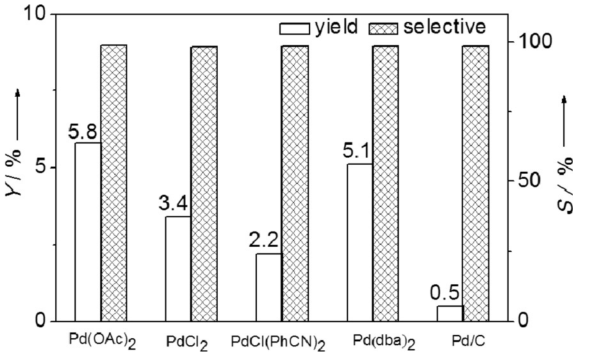


Figure 1. Catalytic performance of different Pd catalysts in the aerobic oxidative coupling of benzene to biphenyl. Conditions: benzene (30 mmol), catalyst (0.022 mmol, 0.07 mol%), acetic acid (6 mL), H$_2$O (4 mL), O$_2$ (3 atm), 105 °C, 7.5 h, GC yield.

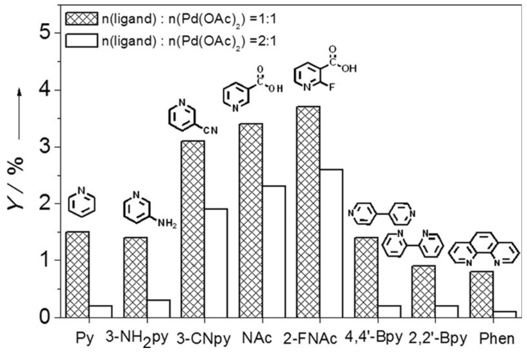


Figure 2. Effects of ancillary ligands on the yield of the Pd(OAc)$_2$-catalyzed aerobic oxidative coupling of benzene to biphenyl over Pd(OAc)$_2$. Conditions: benzene (30 mmol), Pd(OAc)$_2$ (0.022 mmol, 0.07 mol%), ligand (0.022 mmol or 0.044 mmol), acetic acid (6 mL), H$_2$O (4 mL), O$_2$ (3 atm), 105 °C, 7.5 h, GC yield.

cies. The addition of certain ligands is an alternative to prevent the formation of palladium black; nonetheless, a trace or low yield of biphenyl was observed with the use of ligands such as pyridine (py), 3-aminopyridine (3-NH_2py3), 3-cyanopyridine (3-CNpy), nicotinic acid (NAc), 2-fluoronicotinic acid (2-FNAc), 4,4′-bipyridine (4,4′-Bpy), 2,2′-bipyridine (2,2′-Bpy), or 1,10-phenanthroline (Phen; Figure 2). The more ligand used, the more apparent the inhibition. This can be ascribed to the strong electron-donating effect of these ligands to the Pd^{II} species, whereas strong donor effects would decrease the electrophilicity of the Pd^{II} center, which is crucial for the catalytic process of the coupling of benzene to biphenyl.[31] A significant increase of the biphenyl yield occurs upon the addition of organic acids, such as TfOH, TsOH, methanesulfonic acid (MSA), TFA, or trifluoroethanol (TFE), into the $Pd(OAc)_2$ catalytic system (Table 1, entries 3–8). Among these organic acids, TfOH as an additive gives a high yield of 25.3 % and a selectivity of 98 % for biphenyl (Table 1, entry 3). The corresponding TON value is as high as 180, which is far superior to all of the catalytic systems reported previously for the aerobic coupling of benzene to biphenyl.[19–26] Benzoic acid (BEA) and phthalic acid (PTA) lead to inferior activities (Table 1, entries 9 and 10) because of their strong coordination capacity for Pd^{II} that can reduce the electrophilicity of the Pd^{II} center. Without $Pd(OAc)_2$, only a trace amount of biphenyl (<0.5 %) forms in the presence of TfOH (Table 1, entry 4), which suggests that TfOH alone is hardly able to catalyze the coupling reaction. Instead of TfOH as the additive, its sodium salt sodium trifluomethanesulfonate (NaOTf) exhibits a poor yield of 3.1 % and a TON of 22 (Table 1, entry 11), which implies that the strong acidity of TfOH plays an important role in the coupling reaction.

Catalytic performance of the $Pd(OAc)_2$-TfOH system

The aerobic coupling of benzene to biphenyl catalyzed by $Pd(OAc)_2$-TfOH under different reaction conditions is shown in Figure 3. The effects of the solvent composition, catalyst amount, TfOH concentration, oxygen pressure, reaction time, and reaction temperature are systematically examined. The selectivity for biphenyl is kept within the range of 94–98 %, and a small amount of phenol is detected as the byproduct.

Various solvents are tried in the reaction. Only aqueous acetic acid solution is active as the solvent for the generation of biphenyl, and no activity was observed upon using aqueous solutions of ethanol, acetonitrile, DMF, DMSO, or mixtures of ethanol/acetic acid or acetonitrile/acetic acid as solvents. The influence of the composition of the aqueous acetic acid solution on the biphenyl yield is investigated by varying the molar ratio of water to acetic acid (HOAc) with the total solvent volume fixed at 10 mL (Figure 3 A). No biphenyl can be produced by using pure water as the solvent, and a low biphenyl yield (4.6 %) is obtained by using pure acetic acid. In contrast,

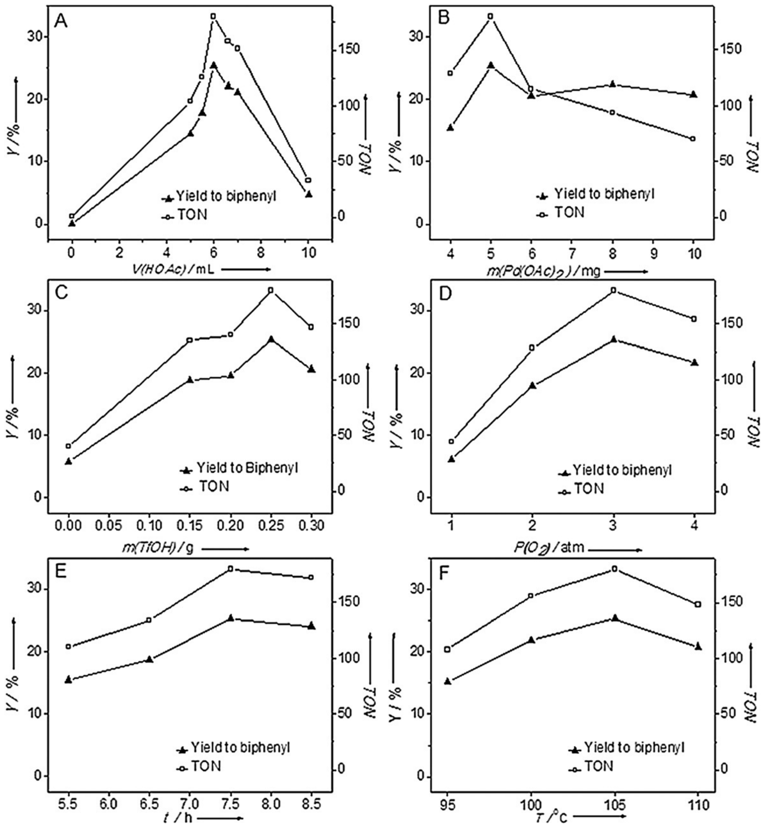
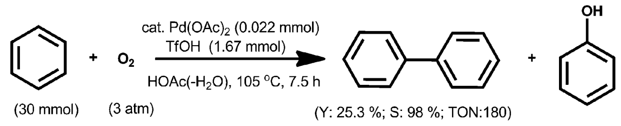


Figure 3. Influences of A) acetic acid volume, B) $Pd(OAc)_2$ amount, C) TfOH amount, D) O_2 pressure, E) reaction time, and F) reaction temperature. Conditions: benzene (30 mmol), $Pd(OAc)_2$ (0.022 mmol, 0.07 mol%), TfOH (0.25 g), acetic acid (6 mL), H_2O (4 mL), O_2 (3 atm), 105 °C, 7.5 h. For each plot, a specific parameter is changed.

the high yield of 25.3 % is achieved by using a certain concentration of aqueous acetic acid solution (acetic acid/H_2O 6:4 v/v); however, an increase of the amount of water or acetic acid will cause a decrease of the biphenyl yield. During the reaction, a homogeneous solution is obtained with acetic acid, whereas a biphasic system forms using aqueous acetic acid solution, the upper phase of which is benzene and the bottom phase is water. The composition of the aqueous acetic acid solution affects the acidity/basicity and the solubility of the substrate, catalyst, and products significantly, from which the mixed solvent influences the mass transfer across the phase and the accessibility of the catalytic species to the substrate, and ultimately results in a different catalytic performance.[39,40] Besides, the addition of water will promote the slow elimination of H^+ from the Wheland intermediate, the control step in the formation of biphenyl, which thus enhances the reaction.[21] Nonetheless, too much water will decrease the benzene solubility in the catalytic phase dramatically, which thus causes a decrease in the reactivity. No product forms in pure water because of the immiscibility of benzene and $Pd(OAc)_2$ in water.

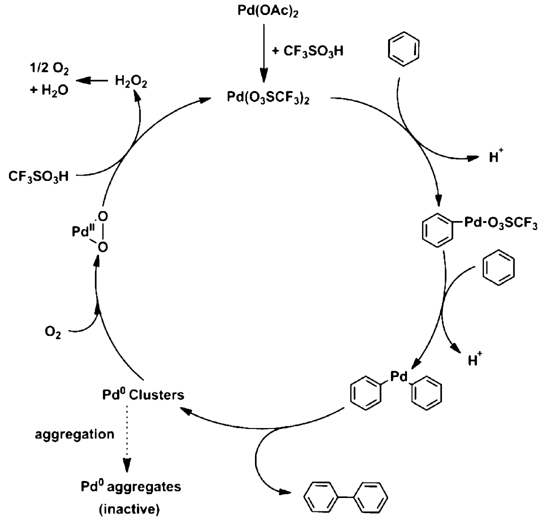
The influence of the catalyst amount on the yield of biphenyl and the corresponding TON values are shown in Figure 3 B. A low amount of $Pd(OAc)_2$, 4 mg, for example, gives a biphenyl yield of 15.3 % and a TON of 129. An increase of the catalyst amount to 5 mg led to an increase of the yield and TON to 25.3 % and 180, respectively. A further increase of the catalyst amount causes a slight decrease of yield and TON. In the oxidative environment of this reaction, the target product biphenyl may be oxidized excessively because biphenyl is more reactive than the substrate benzene. The byproduct formed by overoxidation may be light polycyclic aromatic hydrocarbons that are undetectable by GC. A higher amount of catalyst will promote excessive oxidation into byproducts, which thus decreases the yield and TON of biphenyl. Therefore, the catalyst amount is fixed at 5 mg in the following tests. The influence of the TfOH amount is shown in Figure 3 C. At a low concentration of TfOH, the yield and TON increase continuously with the increase of the concentration of TfOH, and the maximum is achieved at 0.25 g of TfOH. A further increase of the TfOH amount causes a decrease of the yield and TON. A similar influential trend is observed by varying the oxygen pressure, reaction temperature, and reaction time (Figure 3 D–F). In general, the solubility of oxygen in water increases with the oxygen pressure, therefore, a high oxygen pressure leads to a high biphenyl yield. From these results, the optimum conditions for our $Pd(OAc)_2$-TfOH catalytic system are (Scheme 1): benzene (30 mmol), $Pd(OAc)_2$ (0.022 mmol, 0.07 mol %), TfOH (0.25 g, 1.67 mmol), acetic acid (6 mL), H_2O (4 mL), O_2 (3 atm), 105 °C, 7.5 h, under which a high yield to biphenyl of 25.3 % with a TON of 180 is obtained.



Scheme 1. $Pd(OAc)_2$-TfOH catalyzed aerobic oxidation of benzene to biphenyl.

Insight into catalytic behavior of $Pd(OAc)_2$-TfOH

It has been proposed that the coupling of benzene to biphenyl involves five steps (Scheme 2): 1) $Pd(OAc)_2$ is treated with TfOH to obtain the active species $Pd(O_3SCF_3)_2$,[37] 2) electrophilic substitution of arene by Pd^{II} to form the σ-arylpalladium(II) intermediate,[33] 3) formation of biphenyl Pd species through the interaction of the σ-arylpalladium(II) intermediate with another benzene, 4) reductive elimination of biphenyl Pd species to generate the biphenyl product and the Pd^0 species,[22,25] 5) regeneration of Pd^{II} through the oxidation of Pd^0 species by O_2 in the presence of TfOH to complete the catalytic cycle.[41,42] In this step, Pd^0 species interacted with O_2 to form palladacycle(II) species, which dissolved to generate $Pd(O_3SCF_3)_2$ and H_2O_2 with the aid of CF_3SO_3H; subsequently, the formed H_2O_2 decomposed to water and O_2.[43] During the above processes, the aggregation of Pd^0 will deactivate the catalyst in the absence of O_2.



Scheme 2. Plausible mechanism for the catalytic system of $Pd(OAc)_2$-TfOH in the aerobic oxidative coupling of benzene to biphenyl.

Of the five steps, the cleavage of C–H bonds has been proved to be the control step.[21] The introduction of TfOH can facilitate the generation of more electropositive $Pd(O_3SCF_3)_2$ species, similar to the formation of $Pd(O_2CCF_3)_2$ if $Pd(OAc)_2$ was treated with CF_3COOH.[36,40,44] Compared with $Pd(OAc)_2$, the $Pd(O_3SCF_3)_2$ species forms the σ-benzene-Pd complex through the electrophilic substitution of C–H bonds more easily because of the enhanced electrophilic properties. To support this speculation, theoretical calculations by DFT and UV/Vis absorption spectroscopy are conducted.

DFT is performed to explore the charge distribution of the possible compounds $Pd(CF_3SO_3)_2$, $Pd(CH_3SO_3)_2$, $Pd(CF_3COO)_2$, $Pd(CF_3CH_2O)_2$, and $Pd(OAc)_2$ (Figure 4). The results indicate that the charge values of the upper O atoms in these anions are

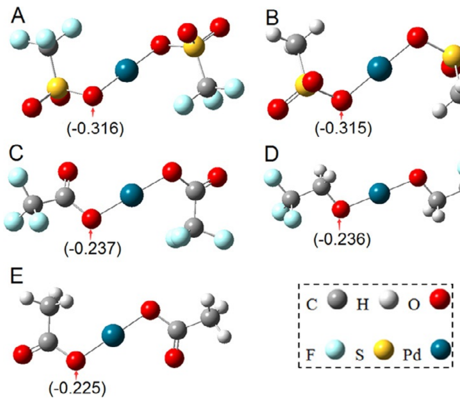


Figure 4. Charge distribution on the Pd compounds, A) $Pd(CF_3SO_3)_2$, B) $Pd(CH_3SO_3)_2$, C) $Pd(CF_3COO)_2$, D) $Pd(CF_3CH_2O)_2$, and E) $Pd(OAc)_2$, calculated by DFT.

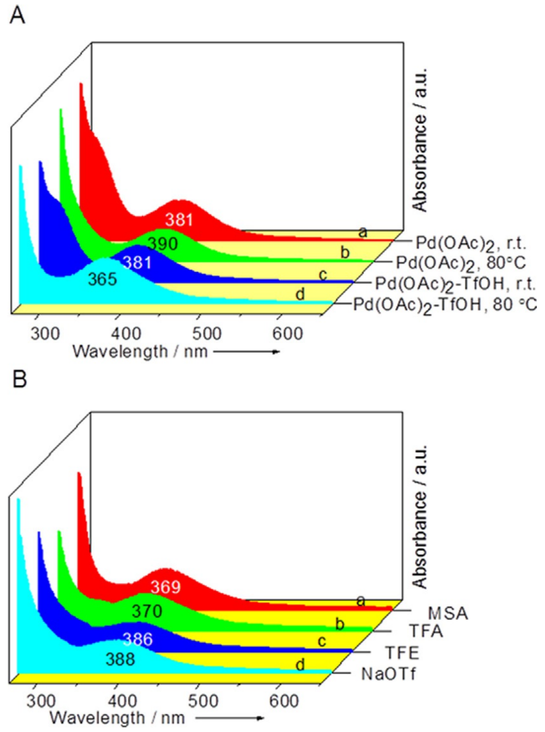
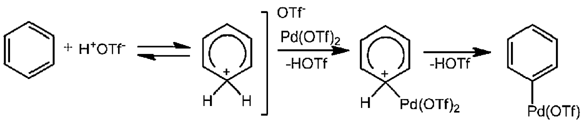


Figure 5. UV/Vis absorption spectra of $Pd(OAc)_2$ (5 mg) in aqueous acetic acid solution (10 mL, 60 vol% acetic acid) pretreated under various conditions. A) $Pd(OAc)_2$ solution pretreated at a) RT and b) 80 °C; with TfOH pretreated at c) RT and d) 80 °C; B) $Pd(OAc)_2$ solution with a) MSA, b) TFA, c) TFE, and d) NaOTf pretreated at 80 °C.

−0.316 for $Pd(CF_3SO_3)_2$, −0.315 for $Pd(CH_3SO_3)_2$, −0.237 for $Pd(CF_3COO)_2$, −0.236 for $Pd(CF_3CH_2O)_2$, and −0.225 for $Pd(OAc)_2$. In other words, the order of the electronegativity of the upper O atoms in these anions is $Pd(CF_3SO_3)_2 > Pd(CH_3SO_3)_2 > Pd(CF_3COO)_2 > Pd(CF_3CH_2O)_2 > Pd(OAc)_2$. The more negative O atom will promote the electrophilic properties of Pd^{II} in the $Pd^{II}L_2$ species, which is more conducive to initiate the electrophilic substitution with benzene. According to this analysis, the order of the activity of these Pd^{II} compounds is $Pd(CF_3SO_3)_2 > Pd(CH_3SO_3)_2 > Pd(CF_3COO)_2 > Pd(CF_3CH_2O)_2 > Pd(OAc)_2$ theoretically, which is consistent with the reaction results.

UV/Vis absorption spectroscopy is performed on $Pd(OAc)_2$ (5 mg) in aqueous acetic acid solution (10 mL, 60 vol% acetic acid) with different acidic additives and pretreated at either room temperature or 80 °C, and the results are shown in Figure 5 A. There are two bands in the spectrum of the additive-free $Pd(OAc)_2$ solution pretreated at room temperature for 7.5 h, that is, a band at $\lambda = 270$–300 nm attributed to the internal $\pi \rightarrow \pi^*$-type transitions of the ligand AcO^-, and another centered at $\lambda = 381$ nm indicative of ligand-to-metal charge transfer (LMCT), which is expected to take place from the acetate ligands to the Pd ions.[45] A similar spectrum is observed upon the addition of TfOH (1.67 mmol) and pretreatment at room temperature for 7.5 h. However, the pretreatment of the $Pd(OAc)_2$ solution at 80 °C causes the disappearance of the band at $\lambda = 270$–300 nm and the redshift of the other band from $\lambda = 381$ to 390 nm, which suggests a more electron-rich Pd^{II} species after treatment at the high temperature close to the actual reaction situation. In contrast, a significant blueshift of the band from $\lambda = 390$ to 365 nm occurs upon the addition of TfOH (1.67 mmol) into the above solution pretreated at 80 °C, which implies a less-electron-rich Pd^{II} species,[46] in other word, the formation of the more electropositive $[Pd^{II}O_3SCF_3]^+$ species.

UV/Vis absorption spectra are also collected from $Pd(OAc)_2$ solutions with other acidic additives again pretreated at 80 °C. The band centered at $\lambda = 390$ nm shifts to $\lambda = 369$ and 370 nm for the $Pd(OAc)_2$ solution in the presence of MSA and TFA, respectively, (Figure 5 B) similar to the $Pd(OAc)_2$-TfOH solution. Such a phenomenon reveals the formation of more electropositive Pd^{II} species, in accordance with catalysis results of enhanced biphenyl yields. A slight blueshift occurs upon the addition of TFE, which suggests the weak influence of this additive on the Pd^{II} state. This result agrees with the observed slight increase of the biphenyl yield if TFE is added. No apparent variation is observed with the addition of NaOTf, which indicates that the additive NaOTf is unable to promote the generation of more electropositive Pd^{II} species that can enhance the activity. This feature accounts for the poor catalytic performance of NaOTf shown in entry 9 of Table 1. The UV/Vis spectroscopy confirms the formation of more electropositive Pd^{II} species upon the addition of some acidic additives with TfOH as the most typical, which would induce the formation process toward biphenyl at high temperature. A more apparent blueshift in the UV/Vis spectra indicates more electropositive Pd^{II} species, and a higher biphenyl yield results from electropositive Pd^{II} species. The results of the UV/Vis absorption spectra are consistent with the results of the DFT calculations, which support our initial speculation [Eq. (1)].



(1)

As previous studies have demonstrated that strong acids favor the coupling reaction,[12,13] the strong acidity of TfOH here also contributes to the high yield of biphenyl. The order of the acid strength of the additives used in this work is TfOH ($pK_a = -15$) > MSA ($pK_a = -1.2$) > TFA ($pK_a = 0.2$) > TFE ($pK_a = 12.4$) > H_2O ($pK_a = 15.7$) in accordance with the activity sequence of TfOH > MSA > TFA > TFE. A low yield is obtained with the use of NaOTf instead of TfOH, which further confirms the important role of acid strength. Moreover, the substrate can be protonated by TfOH, and TfOH can facilitate the formation of the Wheland complex and the subsequent aryl-Pd intermediate through the initial activation of the C–H bond by its protonation [Eq. (1)].[47,48] With the use of $Pd(OAc)_2$ alone (i.e., in the absence of any additives), the appearance of palladium black (Pd^0 species) is observed, therefore, in this case the regeneration of Pd^{II} seems to be a determining step for the deactivation of palladium black. For this reason, in various previous studies some cocatalysts were introduced to help the regeneration of Pd^{II}.[19–26] In this work, the catalytic system of $Pd(OAc)_2$-TfOH leads to no observable palladium black, which suggests that the introduction of TfOH may inhibit the aggregation of Pd^0 species and promote the regeneration of Pd^{II}, which thus ultimately advances the whole catalytic cycle.

Conclusions

A highly efficient catalytic system is developed for the direct aerobic oxidative coupling of benzene to biphenyl with the C–H activation strategy. This Pd-catalyzed oxidative coupling reaction is accomplished in aqueous acetic acid with the aid of trifluoromethanesulfonic acid (TfOH) with oxygen as the sole oxidant. A high yield (25.3 %), selectivity (98 %), and an excellent turnover number of $Pd(OAc)_2$ (180) are observed under the following reaction conditions: benzene (30 mmol), $Pd(OAc)_2$ (0.022 mmol, 0.07 mol %), TfOH (1.67 mmol), acetic acid (6 mL), H_2O (4 mL), O_2 (3 atm), 105 °C, 7.5 h. Organic acids such as TfOH show an excellent efficiency in the aerobic coupling of benzene to biphenyl. No other cocatalyst is required to promote the recycling of $Pd(OAc)_2$. The high yield and turnover number are achieved with the use of a low concentration of $Pd(OAc)_2$ (0.07 mol %), which enables the high efficiency of the noble-metal Pd catalyst.

Experimental Section

Materials

All solvents and reagents were purchased commercially and used without further purification. $Pd(OAc)_2$ (99.9 % metals basis) and TfOH (98 %) were purchased from Aldrich.

Catalytic test

The direct oxidative coupling reaction of benzene with O_2 was performed by using a customer-designed, temperature-controlled, pressurized stainless-steel reactor (25 mL) equipped with a mechanical stirrer. Typically, $Pd(OAc)_2$ (0.022 mmol, 5 mg), benzene (30 mmol, 2.66 mL), and TfOH (1.67 mmol, 0.25 g) were added successively into an aqueous solution of acetic acid (10 mL, 60 vol % acetic acid). The reactor was charged with 3.0 atm O_2 at RT, heated to 105 °C, and stirred for 7.5 h. The reaction products were extracted with a mixture of H_2O and CH_2Cl_2 (1:1 volume ratio) and analyzed by GC (Agilent, 6890B) with a flame ionization detector (FID) and a capillary column (HP-5; 30 m × 0.32 mm × 0.25 μm). 1,4-Dioxane was used as the internal standard.

DFT calculations

DFT calculations were performed by using the Gaussian 09 program suite with the B3LYP[49–51] functional with the 6–311G basis set.[52] The complexes were optimized in the gas phase, and the optimized structures were subsequently subjected to a single-point energy calculation.

UV/Vis absorption spectroscopy

UV/Vis spectra of $Pd(OAc)_2$ in aqueous acetic acid solution were obtained by using a PerkinElmer Lambda 35 diode array spectrophotometer. The solutions for UV/Vis measurements were prepared by dissolving $Pd(OAc)_2$ (5 mg) in aqueous acetic acid (10 mL, 60 vol % acetic acid) that contained different additives (1.67 mmol) and then stirred at RT or 80 °C for 7.5 h.

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