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PdCuCeO-TPAB: A new catalytic system for quasi-heterogeneous Suzuki-Miyaura cross-coupling reaction under ligand-free conditions in water.

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In this contribution, we report a simple and clean method for preparation of a single-phase $Pd_{0.04}Cu_{0.04}Ce_{0.92}O_{2-\delta}$ (PdCuCeO) solid-solution oxide and its application in quasi-heterogeneous Suzuki-Miyaura cross-coupling reactions. The catalyst was characterised fully and all the characterisation techniques strongly suggest that the Pd^{2+} and Cu^{2+} ions were succesfully incorporated into the lattice of ceria. The as-prepared PdCuCeO solid-solution oxide was tested on Suzuki-Miyaura cross-coupling reactions under ligand free conditions using water as a sole solvent and tetrapropylammonium bromide (TPAB) as a phase tranfer catalyst. It was discovered that TPAB acts as scavenger of Pd and the resulting material (Pd/TPAB) is able to catalyse the Suzuki-Miyaura coupling reaction. The Suzuki-Miyaura coupling of aryl iodides, bromides as well as activated aryl chlorides was efficiently performed by this PdCuCeO-TPAB catalytic system. The PdCuCeO-TPAB catalytic system also displayed good functional group tolerance and good to excellent isolated yields were obtained. Catalyst leaching and recyclability studies revealed that PdCuCeO acts as a Pd reservoir and that the reactions are essentially quasi-heterogeneous occuring over the recoverable Pd/TPAB aggregates. Only a negligible amount of palladium (<0.1 ppm) was detected by ICP-OES in the product solution.

Introduction

The Suzuki–Miyaura (SM) cross-coupling reactions are characterized by the cross coupling of an organohalide or organotriflate and an aryl boronic acid to give a biaryl compound.[1-3] The SM cross-coupling reaction has become a useful strategy for the preparation of substituted biaryl compounds, which are essential building blocks for agricultural, pharmaceutical and engineering material industries.[4-10] The 2010 Nobel Prize in Chemistry, awarded to Akira Suzuki, Richard Heck and Ei-ichi Negishi, further demonstrated the significance of Pd-catalyzed cross coupling reactions.[11] Given the applicability of the SM reactions, the design of a more sustainable procedure that uses inexpensive and easily prepared catalysts, environmentally friendly solvents and avoids the use of expensive ligands remains a goal of high practical value.[12]

There is also a growing interest to finding a suitable replacement for palladium with cheaper metals such as iron, copper and nickel.[13] Moreover, Cu(I) salts and Cu_2O have been reported as co-reagents and co-catalysts in SM coupling reactions.[14-19] However, we think it is of equal importance to determine whether palladium catalysts can be better utilised to broaden their impressive reactivity.[20] Notably, Pd catalysts often display a higher reactivity than their alternatives, which enable them to easily catalyze less reactive substrates and achieve high catalyst turnover numbers (TONs).[21] Furthermore, bimetallic nanoparticles supported on carbon (Pd-Cu/C, Pd-Ni/C and Pd-Ag/C) have also shown activity in SM coupling reactions.[22] The catalytic efficiency based on the yield of the desired product decreased in the following order: Pd-Cu/C > Pd/C > Pd-Ag/C > Pd-Ni/C.[22,23] Thathagar *et al.* also observed that the combined Pd/Cu nanoclusters displayed the highest activity among all the other combinations (Pd/Pt and Pd/Ru nanoclusters).[14]

Herein, we further investigated the Pd and Cu combination using the $Pd_{0.04}Cu_{0.04}Ce_{0.92}O_{2-\delta}$ (PdCuCeO) solid-solution oxide, instead of Pd-Cu/C or Pd/Cu nanoclusters, as a bimetallic catalyst for SM reactions. We have previously shown that substitution of Pd^{2+} and Cu^{2+} ions within the CeO_2 lattice allows for complete palladium and copper dispersion, which, as a result, increased the catalyst activity in CO oxidation.[24,25] In addition, we also showed that the synergetic effect between palladium, copper and cerium ions improves the catalyst reducibility and as a result, it enhanced its performance in CO oxidation.[24] For this contribution, we wanted to further exploit the synergetic effect between Pd-Cu-Ce to hopefully enhance the reactivity of PdCuCeO in SM cross-coupling reactions.

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Recently, a wealth of literature has been reported on supported Pd catalysts that catalyze SM cross-coupling reactions with high reactivity, good recyclability and minimal metal leaching.[6-11,26-41] However, the nature of the true catalyst is still unclear and the dominant view at present is that the mechanism of most C-C cross-coupling reactions is largely homogeneous irrespective of the type of catalyst precursor used.[42-49] Hence, the challenge of distinguishing heterogeneous from homogeneous catalysis when heterogeneous systems are developed is still a critical topic.[7,9,42,50]

In this regard, we now report a “greener” and highly efficient procedure that can quasi-heterogeneously catalyse SM coupling using an easily prepared PdCuCeO solid-solution oxide that can be recovered and reused at end of the reaction. In addition, we have eliminated the need for a ligand and utilise water as the sole solvent, since it is cheap, safe and environmentally friendly.[27,31] We also investigated the true nature of catalysis for this SM reaction by doing selective poisoning and hot-filtration tests.

Results and discussion

The solution combustion synthesis method was used to prepare the bimetallic $Pd_{0.04}Cu_{0.04}Ce_{0.92}O_{2-\delta}$ (PdCuCeO) solid-solution oxide. This synthesis method was preferred because it is a relatively simple, quick and inexpensive method for synthesizing highly crystalline and pure noble metal substituted oxides.[51-54] We have recently shown the structural and electronic properties of this material using X-ray diffraction (XRD), XPS, XANES, Raman spectroscopy, EXAFS and high-resolution transmission electron microscopy (HR-TEM).[24] The Rietveld refinement fits of XRD data for PdCuCeO correspond only to the ceria phase with the fluorite structure (JCPDS 34-0394). The absence of the PdO and CuO phases in the X-ray pattern of PdCuCeO supports its phase purity and also strongly suggests that Pd^{2+} and Cu^{2+} ions were successfully incorporated into the ceria lattice (Figure 1).

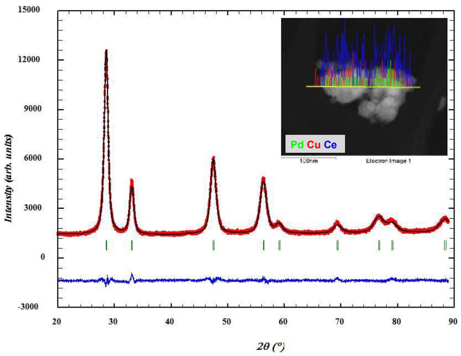

Figure 1: The Rietveld refined XRD patterns of PdCuCeO and its STEM-EDX image (insert)

The STEM-EDX (Figure 1, insert) confirmed the presence of Pd and Cu in the as-prepared PdCuCeO and also shows that both metals are homogeneously dispersed in the ceria lattice.

We also synthesised two monometallic ionic solid-solution oxides ($Pd_{0.04}Ce_{0.96}O_{2-\delta}$ [PdCeO] and $Cu_{0.04}Ce_{0.96}O_{2-\delta}$ [CuCeO]) as control materials. The chemical composition and some physicochemical properties of the studied materials are summarised in Table 1 and the rest of the characterisation data (XRD, XPS, TEM, SEM, EDS, TGA, BET, TPR and Raman spectroscopy) is enclosed in the electronic supplementary information (ESI). The Williamson-Hall method was used to estimate the average crystallite sizes of the prepared solid-solution oxides.[24] The three materials have similar physical properties, their surface areas ranges between 31-34 m^2/g, while their crystallite sizes range from 11-14 nm (Table 1).

Table 1: Physicochemical properties of prepared materials.

Catalyst	Metal loading (wt%)		Crystallite size (nm)	Surface area (m^2/g)
	Pd	Cu		
CuCeO	-	1.8	14	31
PdCeO	2.9	-	14	33
PdCuCeO	3.1	1.7	11	34

Assessment of catalyst activity

The catalyst testing studies began by assessing the effect of several variables on catalyst activity using iodobenzene and phenylboric acid as model coupling partners. First, water was chosen as the reaction medium, since one of our aims was to eliminate organic impurities and use water as sole solvent. We then investigated commonly used inorganic bases (K_2CO_3, Na_2CO_3, Cs_2CO_3, NaOH and *t*-BuOK) in the Suzuki-Miyaura coupling reactions. All the tested bases, except NaOH, gave identical results and Na_2CO_3 was chosen since it is the most commonly used base.[55] It was later realized that for bromoarenes and chloroarenes, the reactions don’t proceed efficiently in the absence of a phase transfer catalyst, tetrapropyl ammonium bromide (TPAB).[56-59] Hence, all the reactions were carried out in the presence of TPAB to allow for a good comparative study (Table 2).

Temperature and catalyst loading were also optimized and the optimum reaction conditions found are summarized in Table 3. There was no reaction at room temperature, while the reaction went to completion in an hour at 60 and 100 °C (Table 2). Further testing was carried out at 100 °C to allow for better miscibility of less water-soluble substrates and better reactivity for difficult substrate such as chloroarenes.

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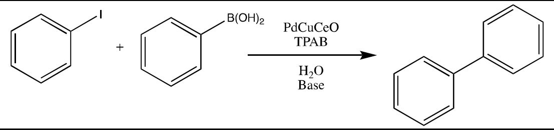
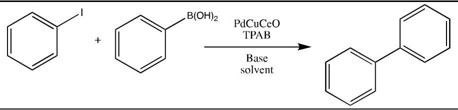
Table 2 Optimisation of reaction conditions



Entry[a]	Base	Catalyst loading (mol% Pd)	Temp. (°C)	Reaction time (h)	Yield (%)[c]
1	*t*-BuOK	0.5	100	1	100
2	K_2CO_3	0.5	100	1	100
3	Cs_2CO_3	0.5	100	1	100
4	Na_2CO_3	0.5	100	1	100
5	NaOH	0.5	100	3	100
6	TPAB	0.5	100	8	10
7	Na_2CO_3	0.5	60	1	100
8	Na_2CO_3	0.5	25	12	0
9[b]	Na_2CO_3	0.1	100	2	100
10[b]	Na_2CO_3	0.05	100	2	100

[a] Volume of water = 2 mL
[b] Volume of water = 5 mL
[c] GC yield

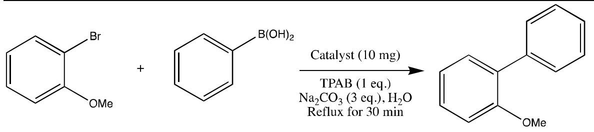
Table 3 Optimum reaction conditions



Reaction conditions	
Solvent	H_2O (5 mL)
Base	Na_2CO_3 (3 eq.)
Temperature	100 °C
Catalyst loading (Pd based)	0.05 mol%
Additive	TPAB (1 eq.)

Under the obtained optimum reaction conditions (Table 3), several control reactions were carried out using 2-bromoanisole and phenylboric acid as model coupling partners. 2-Bromoanisole is a highly deactivated coupling partner, thus it allows for a more reliable determination of the most robust catalytic system. The results showed that no reaction occurs in the absence of a palladium containing catalyst (Table 4). In addition, the palladium and copper containing catalyst (PdCuCeO) was the superior catalyst. Firstly, the data suggests that palladium is the active metal; secondly, it suggests that there is a synergetic effect between palladium and copper ions, since PdCuCeO was more active than PdCeO, while CuCeO was inactive. Hence, the synergetic effect between palladium and copper in PdCuCeO improves its catalyst performance. Further catalytic testing was thus carried out using the PdCuCeO solid-solution oxide.

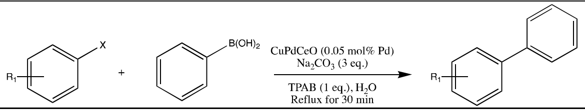
Table 4 Investigating the most robust catalyst for SM cross-coupling reactions under optimum reaction condition.



Entry	Catalyst	% Yield
1	No catalyst	No reaction
2	CuCeO	No reaction
3	PdCeO	20
4	PdCuCeO	48

To establish the versatility of the developed PdCuCeO catalyzed SM coupling reactions, the reactions of phenylboronic acids with iodoarenes, bromoarenes, and chloroarenes were further studied; the results are summarized in Tables 5 and 6. To allow for a good comparative study, the reaction time was fixed at 30 minutes, since using water as a sole solvent meant that we couldn't reliably and quantitatively monitor the progress of the reaction due to limited solubility of some subtrates and products in the reaction medium.

Table 5 SM cross-coupling of iodo- and bromoarenes with phenylboric acid to give substituted biphenyls under our optimum reaction conditions



Entry	R_1—	X	% Yield	TOF /h^{-1}
1	H	I	85	2797
2	4-NH_2	I	62	2010
3	4-Me	I	72	2338
4	4-COH	I	100	3308
5	4-COMe	I	100	3308
6	3-CF_3	I	100	3308
7	4-NO_2	I	100	3308
8	H	Br	80	2630
9	4-Me	Br	73	2402
10	2-OMe	Br	48	1670
11	4-F	Br	88	2890
12	4-COH	Br	100	3308
13	4-COMe	Br	100	3308
14	4-CF_3	Br	100	3308
15	4-NO_2	Br	100	3308

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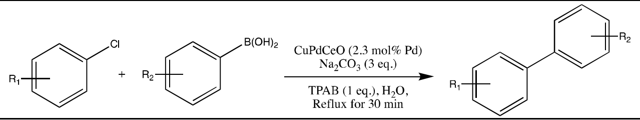
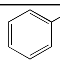
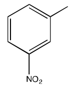
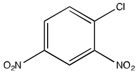
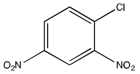
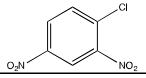
The results show that the PdCuCeO catalysed SM cross-coupling reactions are efficient over a wide range of ortho-, meta- and para-substituted haloarenes and that various functional groups of the substituents are well tolerated. The PdCuCeO catalyst was highly active, achieving TOFs of up-to 3300 h^{-1} (Table 5). It was observed that electron-withdrawing substituents speed-up the reaction (Table 5, Entries 4-7 and 12-15), while electron-donating substituents slow down the catalytic activity (Table 5, Entries 2-3 and 9-10). The highly activated substrates reacted have identical TOFs since their reaction times are less than 30 minutes (which is fixed) and each reaction only yields the desired product.

Due to the success gained from the activation of aryl iodides and bromides, the study was extended to develop a procedure that facilitates efficient SM coupling of chloroarenes (Table 6). The synthesis of fine chemicals and phamaceuticals should benefit highly from the activation of chloroarenes, since these can serve as cheap and readily available starting materials. Unfortunately, chloroarenes are notoriously more difficult to activate than iodo- and bromoarenes. In our initial study we focused on the coupling of unactivated chloroarenes (Table 6, Entry 1), however, sluggish results were obtained even when using 4.6 mol% Pd. Moderate to excellent yields were only obtained from coupling of activated chloroarenes with various phenylboric acids (Table 6, Entry 2-5). The activated chloroarenes also allowed for lower catalyst loading.

Table 6 SM cross-coupling of chloroarenes with various phenylboric acids to give substituted biphenyls

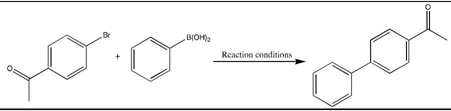


Entry	Chloroarene	R_2	%Yield	TOF /h^{-1}
1[a]		4-H	<5	<4
2[a]		4-Me	42	15
3[b]		4-H	100	34
4[b]		4-Me	100	34
5[b]		4-OMe	100	34

[a] Catalyst loading = 4.6 mol%
[b] Catalyst loading = 2.3 mol%

To evaluate the performance of the developed catalytic system, the product yield (4-acetylbiphenyl) of the present catalytic system was compared to other reported “heterogeneous” and ligand-less palladium catalyzed SM cross-coupling reactions that use water as sole solvent (Table 7). The yield of 4-acetylbiphenyl in this work was found to be comparable or better to most reported yields in literature. Furthermore, the present catalyst system gives superior TONs and TOFs than most reported catalytic systems that use water as a sole solvent (Tables 5 and 7).[12,59-63]

Table 7 Performance comparison of catalytic systems in SM coupling of 4-bromoacetophenone to phenylboric acid under ‘heterogeneous’, ligand-free conditions that use water as a sole solvent.



Entry	Catalyst [mol% Pd]	Reaction conditions	Time /h	Yield[a] /%	Ref.
1	Pd/C [0.05]	H_2O, CTAB, K_2CO_3, @60 °C	4	89 (445)	[60]
2	Pd/polymer [2]	H_2O, K_3PO_4, @100 °C	5	93 (9)	[61]
3	Pd/porous glass [0.45]	H_2O, K_2CO_3, TBAB, MW(300W), @150 °C	0.17	99 (12941)	[62]
4	Pd@SBA-15(C) [0.08]	H_2O, TBAB, K_2CO_3, @80 °C	1	97 (1212)	[63]
5	Pd/HAP [0.33]	H_2O, K_2CO_3, TBAB, @80 °C	4	94 (71)	[12]
6	PdNPs/ZrO_2 [0.1]	H_2O, TBAOH, @90 °C	14	90 (71)	[59]
7	PdCuCeO [0.05]	H_2O, Na_2CO_3, TPAB, @100 °C	0.5	100 (3308)	This paper

[a] Parentheses = TOF/h^{-1}

Catalyst leaching and recyclability studies

The SM cross-coupling reaction is often used by pharmaceutical industries in the synthesis of medicinal compounds. Thus it is important to quantify the residual metal in the product when developing heterogeneous systems. The requirement is that the residual metal must be kept below 5 ppm.[57,64] To distinguish homogeneous from heterogeneous catalysis and possibly determine the true nature of catalysis for these reactions in the present study we conducted a series of investigations: catalyst recovery and recyclability, hot-filtration, selective poisoning tests and elemental analysis of the fresh and used catalyst. Phenylboric acid and 4-bromoacetophenone were used as model coupling partners for all the leaching and recyclability studies.

The catalyst was recovered quantitatively at the end of the reaction and reused three times. It was observed that the catalyst activity dropped with each subsequent recycle (Figure 2). Catalyst deactivation is usually caused by chemical, mechanical and/or thermal degradation of the heterogeneous catalyst. Herein, we only investigated chemical degradation (leaching) of the catalyst, since it is the most common catalyst

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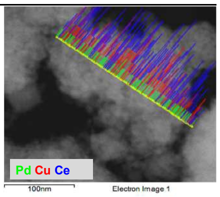
deactivator for these types of reactions and its study could lead to a better understanding of the true nature of the catalysis.[44,57] To investigate the cause of deactivation we conducted elemental analysis of the reaction solution, fresh and used catalyst (Table 8). The metal content of the fresh and used catalyst were compared and it was observed that the fresh catalyst lost about 50% of Pd and Cu in its first use. However, only about 6% of the leached Pd was found in the reaction solution (Table 8).

Table 8 ICP-OES elemental analysis of the fresh and used PdCuCeO catalyst

	Pd loading (wt%)	Cu loading (wt%)	STEM-EDX image of used PdCuCeO
Fresh PdCuCeO	3.1	1.7	
Used PdCuCeO	1.4	0.72	
Reaction solution	<0.1 ppm	3 ppm	

Catalyst poisoning tests were thus performed to further investigate the possible presence of leached, soluble palladium from the PdCuCeO pre-catalyst. This test was performed using ethylpyridine as poison, since pyridines are reported to bind strongly to Pd(II).[44,65] Ethylpyridine was added along with the other reagents at the start of the reaction and then the reaction was stirred under similar conditions. The results in Figure 2 revealed that ethylpyridine addition did partially deactivate the catalyst, since the 4-bromoacetophenone conversion dropped to 40%. Hence, this test confirmed the presence of leached palladium in the TPAB-water mixture.

The hot filtration test was then performed to assess the activity of any leached palladium in the TPAB-water mixture. In the hot filtration test, a mixture of PdCuCeO, 4-bromoacetophenone, phenylboric acid, TPAB and Na_2CO_3 in water was stirred at 100 °C for 5 minutes. The catalyst was filtered off from the reaction mixture after 5 min and the hot filtrate was then allowed to react further for 25 minutes under similar conditions. It was, however, noticed that during the hot filtration a significant quantity of TPAB precipitated out of the solution, hence the filtrate contained little to no TPAB. The results in Figure 2 show negligible activity in the filtrate, suggesting that there is very little soluble Pd present in the solution. The ICP elemental analysis of the filtrate also revealed that there was a very low amount of Pd (<0.1 ppm) left in the filtrate (Table 8). Hence, lack of activity is due to an insufficient amount of Pd in the filtrate to catalyse the Suzuki reaction.

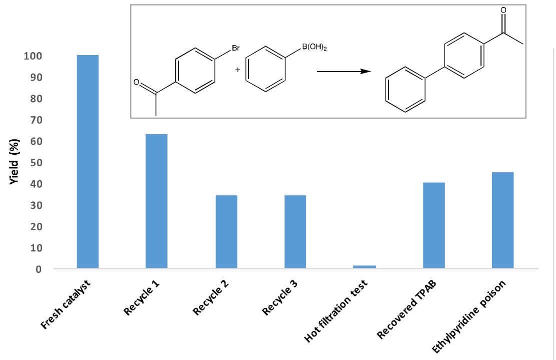
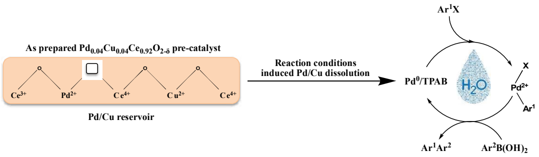


Figure 2 Catalyst leaching and recyclability studies

It was suspected that the Pd might have precipitated out with TPAB, since the ethylpyridine poison test confirmed the presence of Pd in the TPAB-water mixture. This then led us to recover TPAB and test its activity. The recovered TPAB gave about 40% conversion to the desired product. This suggest that TPAB acts as a scavenger of Pd and its aggregates are able to generate, in situ, highly dispersed palladium nanoparticles (Pd/TPAB) from simple PdCuCeO. Hence, the catalyst recyclability and leaching tests performed in the current work agree very well with the findings of other studies using Pd-doped metal oxides as precatalysts, and substantiate the hypothesis that the precatalysts act as a palladium reservoir, that slowly releases extremely reactive Pd species.[37,60] In our case, the released Pd is captured by TPAB and generates, in situ, a highly active quasi-heterogeneous Pd/TPAB catalyst (Scheme 1). We have termed the active catalyst system as PdCuCeO-TPAB. The catalytic cycle is then initiated by the oxidative addition of the aryl halide to palladium to form the organopalladium complex. In the presence of a base, this organopalladium complex reacts with boric acid via a transmetallation step and the desired product is then obtained via the reductive elimination step (Scheme 1). This special type of the Pd release/capture mechanism proved very advantageous, since it has potential to resolve the difficulties of catalyst separation and recovery and it greatly minimizes metal contamination of the products.



Scheme 1 Shows an illustration of the proposed reaction mechanism for the PdCuCeO-TPAB catalysed quasi-heterogeneous SM cross-coupling reactions.

Conclusions

In summary, we have demonstrated that the PdCuCeO-TPAB catalytic system can catalyse the Suzuki-Miyaura cross-coupling under milder and more environmentally friendly reaction conditions. The reactions were conducted in water as sole solvent and the addition of a ligand was unnecessary. The PdCuCeO-TPAB catalytic system also displayed good functional group tolerance and good to excellent isolated yields were

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obtained. Catalyst leaching and recyclability studies revealed that PdCuCeO acts as a Pd reservoir and that the reactions are essentially quasi-heterogeneous, occuring over recoverable Pd/TPAB aggregates. The TPAB aggregates generate, in situ, highly dispersed palladium nanoparticles from simple PdCuCeO. As as result, the PdCuCeO catalytic activity declined with each subsequent recycle. However, only a negligible amount of palladium (<0.1 ppm) was detected by ICP-OES in the product solution because most of the palladium is removed from the reaction solution by TPAB. Hence, this PdCuCeO-TPAB catalytic system has potential to resolve the difficulties of catalyst separation and recovery, since it greatly minimises metal contamination of the products.

Experimental

Cerium ammonium nitrate [$(NH_3)Ce(NO_3)_6$, 99.9%], palladium nitrate [$Pd(NO_3)_2$], copper nitrate [$Cu(NO_3)_2$], and urea [CH_4N_2O, 99.9%] were obtained from Sigma-Aldrich and were used without further purification.

Procedure for synthesis of $Pd_{0.04}Cu_{0.04}Ce_{0.92}O_{2-\delta}$

The monophasic $Pd_{0.04}Cu_{0.04}Ce_{0.92}O_{2-\delta}$ solid-solution oxide was prepared using a one-step urea-assisted solution combustion synthesis method described earlier.[26] The catalyst synthesis method involved preparation of a redox combustion mixture composed of stoichiometric amounts of metal precursors [$(NH_4)_2Ce(NO_3)_6$, $Pd(NO_3)_2$ and $Cu(NO_3)_2$] and urea [NH_2CONH_2] in the ratio of 1.0:3.68 respectively. The solution was then stirred at 150 °C for 10 minutes to evaporate water and reduce its volume to ≈20 mL. The boiling solution was then introduced into a muffle furnace pre-heated at 400 °C and was kept in the furnace for 5 hours. A light grey solid was obtained.

Catalyst testing: general procedure for coupling reactions

A dry two necked pear-shaped flask containing a stirrer bar, a condenser and 5 mL of H_2O was charged with an aryl halide (4.6 mmol), boric acid (2 eq.), Na_2CO_3 (3 eq.) and catalyst $Pd_{0.04}Cu_{0.04}Ce_{0.92}O_{2-\delta}$ (0.05 mol% Pd). The reaction mixture was stirred and (usually) heated to 100 °C and its progress was monitored by GC and GC-MS (the reaction mixture was homogenized with 5 mL of toluene). The aryl halide conversion was used to estimate the catalytic activity, using benzophenone as an internal standard. After the reaction had gone to completion, the reaction mixture was filtered and the filtrate was extracted with ethyl acetate and brine. Pure products were obtained by simple filtration through silica gel using ethyl acetate as solvent. The structure of the coupling product was confirmed by ^{1}H and ^{13}C NMR spectroscopy and the results were consistent with those reported in literature for substituted biphenyls.[8]

General procedure for catalyst recovery and recyclability

The catalyst used in the first run was separated by centrifugation, washed with 5 mL toluene and water, respectively, dried at 60 °C and reused as described for the fresh catalyst.

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Highlights

- PdCuCeO was applied for Suzuki-Miyaura coupling in pure water. The catalyst was highly active (TOF >3000 h^{-1}) and could be reused.