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$Pd_{0.02}Ce_{0.98}O_{2-\delta}$: a copper- and ligand-free quasi-heterogeneous catalyst for aquacatalytic Sonogashira cross-coupling reaction

by P.P. Mpungose, N.I. Sehloko, T. Cwele, G.E.M. Maguire and H.B. Friedrich

Synopsis

A $Pd_{0.02}Ce_{0.98}O_{2-\delta}$ solid solution oxide was synthesised in one step using a urea-assisted solution combustion method. XRD, ICP-OES, BET, XPS, SEM, EDX, TEM, TGA and Raman spectroscopy were used to study the structural and electronic properties of the as-prepared $Pd_{0.02}Ce_{0.98}O_{2-\delta}$ catalyst. The catalyst testing results revealed that the $Pd_{0.02}Ce_{0.98}O_{2-\delta}$ system performs as an efficient precatalyst for the Sonogashira cross-coupling reactions under copper- and ligand-free conditions. A wide range of iodoarenes were efficiently coupled to phenylacetylene with good to excellent isolated yields. A thorough investigation through a series of suitable experiments explicitly showed that the Sonogashira cross-coupling reaction is accomplished via a quasi-heterogeneous mechanism by the leached Pd(0) species. As a result, the $Pd_{0.02}Ce_{0.98}O_{2-\delta}$ lost some activity upon recycling.

Keywords

Pd^{2+} substituted ceria, solution combustion, nanoparticles and Sonogashira coupling reactions.

Introduction

The Sonogashira cross-coupling reaction is a great procedure for C-C bond formation between vinyl or aryl halides and terminal alkynes (Sonogashira, Tohda and Hagihara, 1975; Takahashi *et al.*, 1980; Sonogashira, 2002). Sonogashira, Tohda and Hagihara (1975) recognised that the addition of copper(I) iodide significantly accelerates the alkenylation reaction that was conventionally catalysed by palladium–phosphane complexes (Sonogashira, Tohda and Hagihara, 1975; Takahashi *et al.*, 1980; Sonogashira, 2002). Their discovery engendered great interest since the products of this reaction are important intermediates in the synthesis of organic materials, pharmaceuticals and natural products (Sonogashira, Tohda and Hagihara, 1975; Takahashi *et al.*, 1980; Sonogashira, 2002; Böhm and Herrmann, 2000; Cwik, Hell and Figueras, 2006; Hosseini-Sarvari, Razmi and Doroodmand, 2014; Mujahidin and Doye, 2005; King and Yasuda, 2004). For example, the Sonogashira coupling procedure is used in the synthesis of the drug Terbinafine, which is used as an antifungal agent (Torborg and Beller, 2009; Beutler *et al.*, 1996).

In most cases, the conventional Sonogashira coupling reactions are carried out under homogeneous conditions, which involve using palladium complexes such as $[PdCl_2(PPh_3)_2]$ or $[Pd(PPh_3)_4]$ (3–5 mol%), a catalytic amount of a Cu salt (3-10 mol%) and an amine in large excess (Sonogashira, Tohda and Hagihara, 1975; Sonogashira, 2002; Rosa *et al.*, 2015; Ciriminna *et al.*, 2013). The use of copper salts as co-catalysts accelerates the Sonogashira reaction greatly; however, their presence in the reaction yields alkyne dimers (Sisodiya *et al.*, 2015). This leads to the generation of an undesired homocoupling product of the alkyne upon oxidation. Thus, the reaction must be conducted under inert atmosphere if a Cu salt is to be used as a co-catalyst (Sisodiya *et al.*, 2015). Furthermore, the above-mentioned standard conditions require a high loading of palladium and involve the use of phosphine ligands that are usually oxygen-sensitive (Cwik, Hell and Figueras, 2006). In addition, the efficient separation and subsequent recycling of homogenous palladium catalysts and ligand remains a challenge and an aspect of environmental and economic relevance (Roy, Senapati and Phukan, 2015).

Intensive studies on heterogenization of Sonogashira coupling reactions with the objective of combining the benefits of both heterogeneous and homogeneous catalysis have been carried out during the last three decades (Abu-Reziq and Alper, 2012). In this direction, researchers have immobilised Pd on solid supports such as activated carbon (charcoal) (Rossy *et al.*, 2014), zeolites

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(Djakovitch and Rollet, 2004), metal oxides (Cwik, Hell and Figueras, 2006; Hosseini-Sarvar, Razmi and Doroodmand, 2014; Roy, Senapati and Phukan, 2015; Kotadia *et al.*, 2014) (MgO, ZnO, TiO_2, ZrO_2, Fe_2O_3, CeO_2, .), clays (Borah and Dutta, (2013), alkaline earth salts ($CaCO_3$, $BaSO_4$, $BaCO_3$, $SrCO_3$) (Barros *et al.*, 2008) and organic polymers (Ye and Yi, 2008; Kim *et al.*, 2007). However, the leaching of palladium from the catalyst is still the main problem, even though most researchers have reported that their catalysts can be recycled by the redeposition of Pd onto the support (Redon, Peña and Crescencio, 2014). This is due to the quasi-heterogeneous mechanism of the Sonogashira cross-coupling reaction via the solvated palladium clusters (Reay and Fairlamb, 2015).

Hence, quasi-heterogeneous catalysis has developed into a new stream in catalysis and it is a promising approach for bridging heterogeneous and homogeneous catalysis (Abu-Reziq and Alper, 2012). Quasi-heterogeneous catalysis relies on the fact that nano-supports have a large surface areas, thus they can retain the activity and selectivity of the supported catalysts (Abu-Reziq and Alper, 2012; Wu *et al.*, 2011).

In this regard, we thought it would be worthwhile to develop a general catalytic system for a copper- and ligand-free quasi-heterogeneous Sonogashira coupling reaction catalysed by a nano $Pd_{0.02}Ce_{0.98}O_{2-\delta}$ solid solution oxide. To the best of our knowledge, $Pd_xCe_{1-x}O_{2-\delta}$ based solid-solution oxides have not previously been investigated on the Sonogashira coupling reactions. Using an air, moisture and thermally stable quasi-heterogeneous $Pd_{0.02}Ce_{0.98}O_{2-\delta}$ solid solution oxide should offer higher activity, simplicity of workup, recyclability and minimisation of metallic waste.

Results and discussion

The structural and electronic properties of the $Pd_{0.02}Ce_{0.98}O_{2-\delta}$ catalyst have been deduced earlier by X-ray diffraction (XRD), XPS, XANES, Raman spectroscopy, EXAFS and high-resolution transmission electron microscopy (HR-TEM) (Cwele *et al.*, 2016).The characterisation results indicated that the prepared material was a solid solution oxide with a fluorite structure. The Rietveld refined XRD profile of the prepared catalyst and the XPS of the Pd(3d) are shown in Figure 1. The X-ray pattern corresponds to a monophasic $Pd_{0.02}Ce_{0.98}O_{2-\delta}$ solid-solution oxide with a fluorite structure as reported earlier (Cwele *et al.*, 2016). The insert in Figure 1 shows the XPS of the Pd(3d). The binding energy of Pd($3d_{5/2}$) and Pd($3d_{3/2}$) at 337.5 and 342.5 eV respectively, confirm that Pd is in the +2 oxidation state.

The crystallite size and the lattice strain were estimated employing Williamson-Hall (W-H) plots and Equation [1]. The lattice strain in the $Pd_{0.02}Ce_{0.98}O_{2-\delta}$ sample was four times greater than in the CeO_2 sample (Table I). This indicates that lattice distortion occurs upon introduction of Pd^{2+} ions in the CeO_2 lattice. The average crystallite size increased slightly with the incorporation of the Pd^{2+} ions into the CeO_2 lattice. The average crystallite size of the blank CeO_2 is 8 nm, while that of $Pd_{0.02}Ce_{0.98}O_{2-\delta}$ increased to 13 nm.

$$\beta_{hkl}\cos\theta = \frac{K\lambda}{D} + 4\varepsilon\sin\theta \qquad [1]$$

The SEM and TEM images of CeO_2 and $Pd_{0.02}Ce_{0.98}O_{2-\delta}$ samples have very similar morphology (Figure 2). In both samples, the particles are present in the form of different sized lumps or flakes with rounded shaped structures. These types of structures are generated due to the nature of the solution combustion synthesis method, where gases escape giving rise to porosity. The BET surface area of the $Pd_{0.02}Ce_{0.98}O_{2-\delta}$ sample was found to be 58 m^2/g (Table I).

The catalytic performance of the as-prepared $Pd_{0.02}Ce_{0.98}O_{2-\delta}$ solid-solution precatalyst was evaluated in the Sonogashira coupling of phenylacetylene and various haloarenes and the results are listed in Table II.

Optimisation of reaction conditions was conducted in order to develop a general catalytic system for the copper- and ligand-free $Pd_{0.02}Ce_{0.98}O_{2-\delta}$ catalysed Sonogashira

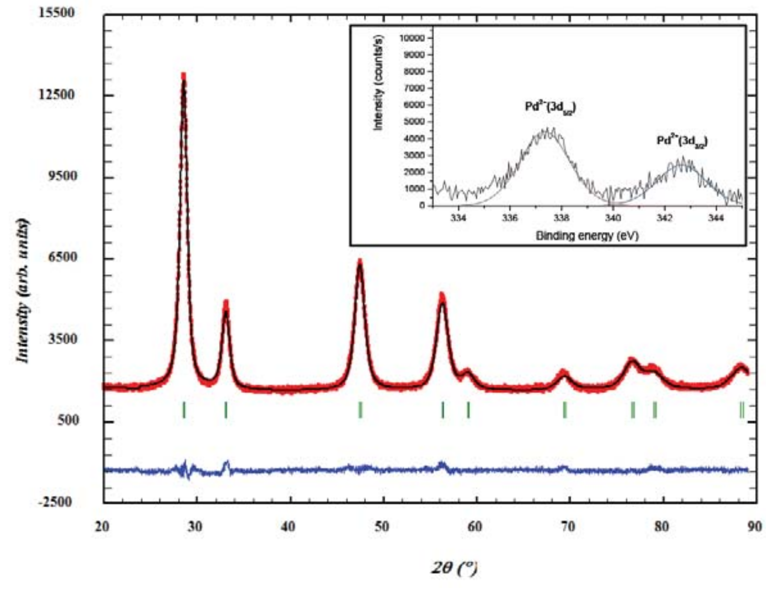


Figure 1—The Rietveld refined XRD patterns of $Pd_{0.02}Ce_{0.98}O_{2-\delta}$ and its XPS of Pd(3d) core level region (inset)

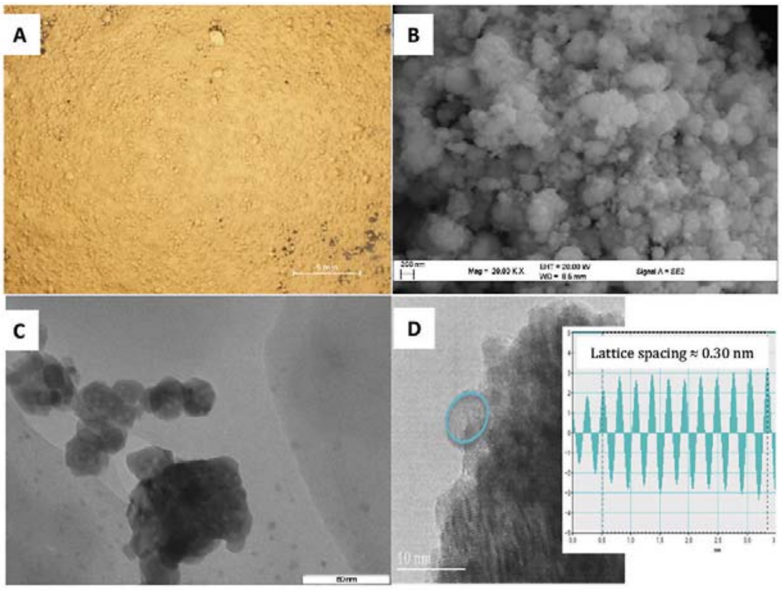


Figure 2—Light microscopy (A), SEM (B), TEM (C) and HR-TEM (D) analysis of the $Pd_{0.02}Ce_{0.98}O_{2-\delta}$ catalyst

Table I

Physicochemical properties of the synthesised materials

Catalyst	Lattice parameter *a* (Å)	Lattice strain (10^{-3})	Crystallite size (nm)	Surface area (m^2/g)
CeO_2	5.4221	1.10	8	69
$Pd_{0.02}Ce_{0.98}O_{2-\delta}$	5.4200	4.20	13	58

Table II

Effect of a base on the model Sonogashira cross-coupling reaction

Entry	Base	Reaction time/h	Conversion/%
1	Cs_2CO_3	24	62
2	Et_3N	1	100
3	K_2CO_3	24	66
4	NaOAc	24	21
5	NaOH	24	48

coupling reaction. Solvent, temperature, alkyne loading, base and catalyst loading investigations were conducted using phenylacetylene (1) and iodobenzene (2) as model coupling partners (Scheme 1, Figure 3).

We first conducted investigations to find a solvent system that is conducive for the Sonogashira coupling reaction (Figure 4). The solvent systems investigated were: acetonitrile (CH_3CN), DMF, toluene (PhMe), 'solvent-less' and H_2O/CH_3CN (1:3 v/v). Toluene gave the lowest conversion of 32% after 8 hours, while 'solvent-free' and acetonitrile conditions gave relatively high conversion, of 68% and 80% respectively. DMF gave 100% conversion in 3 hours, while H_2O/acetonitrile (1:3 v/v) went to completion in an hour. Hence, further investigations were conducted in H_2O/acetonitrile (1:3 v/v). Böhm and Herrmann (2000) reported that the polarity and hydrogen bonding ability of the solvent are important in accelerating the reaction by stabilizing the ionic intermediates of the catalytic cycle. The solvent investigation results agree well with the above statement, since the reaction conducted in toluene has the longest reaction time and the lowest percentage conversion, while those conducted in aqueous acetonitrile had the shortest reaction time and gave 100% conversion of phenylacetylene. The Böhm and Herrmann findings also indirectly address the nature of catalysis for most Sonogashira coupling procedures (discussed later).

The choice of base is considered crucial in Sonogashira coupling reactions. The base is used to neutralise the acid (HX) formed as a by-product in this reaction (Böhm and Herrmann, 2000). In addition, the base plays a role in inhibiting the generation of a homo-coupling product (Glaser-type reaction) and its strength plays a key role in the deprotonation of terminal alkynes (Böhm and Herrmann,

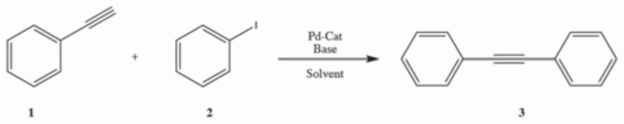


Figure 3—Scheme 1: the model Sonogashira cross-coupling reaction between phenylacetylene (1) and iodobenzene (2) leading to biphenylacetylene (3)

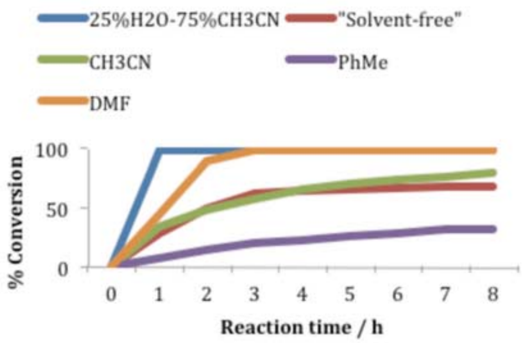


Figure 4—Solvent investigation results under the model Sonogashira coupling conditions

2000; Komura, Nakamura and Sugi, 2008). Among the investigated bases, triethylamine was found to be the best base under our reaction conditions (Table II). The reaction went to completion in just an hour when triethylamine was used as base, but did not go to completion with the other bases investigated (K_2CO_3, NaOH, CH_3COONa and Cs_2CO_3). It has been suggested that amines do not act as bases only, but also as weak coordinating ligands (Jutand, Négri and Principaud, 2005). Hence, beside the observed solubility problem when the inorganic bases were used, the fact that triethylamine can act as a coordinating base is thought to be a major reason for its superior performance.

Three different temperatures were also investigated; 25, 50 and 82°C (Figure 5). It was found that the reactions were most rapid under refluxing conditions (82°C).

Several experiments were conducted to find the lowest amount of the catalyst loading (based on Pd) that could efficiently catalyse the Sonogashira coupling reactions in reasonable reaction times (Figure 6). The investigations were initiated with catalyst loading between 0.05-1 mol%. For loadings of 0.1-1 mol%, the reaction was found to be very fast and the reaction went to completion in an hour. This fast reaction makes it difficult to monitor the substitution and electronic effect caused by the aryl halides. Hence, a catalyst loading of 0.05 mol% was investigated; this then gave a slower reaction that went to completion in 3 hours.

A combination of aryl halides and terminal alkynes was then studied to investigate the scope and limitations of our catalytic system under the obtained optimum reaction conditions. The investigations were initiated by reacting various iodoarenes with phenylacetylene, to investigate the electronic effect and the substitution position effect on the haloarenes.

It was found that the aryl halides with electron-withdrawing groups in the para-position (Table III, entries 4, 5, 9 and 11) react more rapidly compared to those with

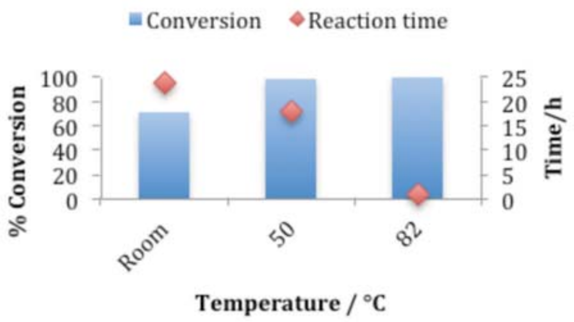


Figure 5—Effect of temperature on the model Sonogashira coupling reaction

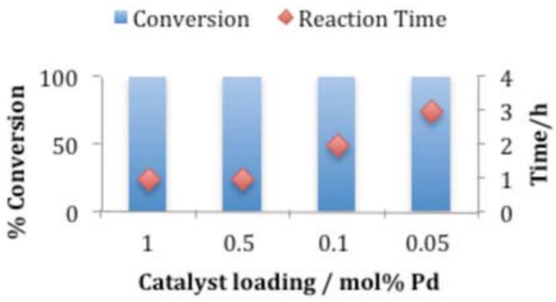


Figure 6—Effect of catalyst loading on the model Sonogashira coupling reaction

electron-donating groups in the same position (Table III, entries 2, 3 and 7). Hence, the electronic effect dictates the catalyst activity in the Sonogashira coupling reactions. It was also noted that the position of each functional group on the aryl halide also controls the activity of the catalyst. This is best demonstrated by the reactivity of 4-iodotoluene and 3-iodotoluene (Table III, entries 7 and 8); where the 3-iodotoluene reacts three times faster than 4-iodotoluene. These findings agree well with the reported influence of substituents in aryl halides on Sonogashira coupling reactions (Sonogashira, Tohda and Hagihara, 1975; Takahashi *et al.*, 1980; Sonogashira, 2002).

With the success obtained with aryl iodides, the reactions were extended to aryl bromides and aliphatic alkynes. However, bromoarenes, chloroarenes and aliphatic alkynes were found to be unreactive under the obtained optimum conditions. The stability of the C–Cl and C-Br bonds makes chloroarenes and bromoarenes notoriously less reactive. Even under homogeneous copper-free coupling reaction conditions, aryl bromides give fairly low conversions (10-60%) (Cwik, Hell and Figueras, 2006).

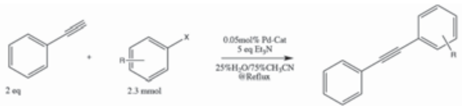
Hence, the obtained optimum conditions are limited to iodoarenes and aromatic alkynes as coupling partners only. Performance comparisons of the present catalyst in Sonogashira cross coupling reactions of iodobenzene and phenylacetylene against other related Cu- and ligand-free catalytic systems are shown in Table IV.

Leaching and recyclability test

A strong test for evaluating heterogeneity of a catalyst is the hot filtration test. To determine whether the reactions reported here were homogeneous or heterogeneous, a hot filtration test was performed for the Sonogashira coupling of

Table III

Sonogashira cross-coupling of phenylacetylene with various iodoarenes to give substituted biphenylacetylenes under our optimum reaction conditions



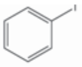
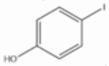
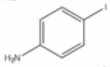
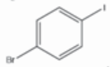
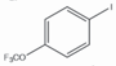
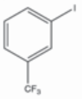
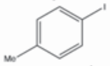
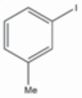
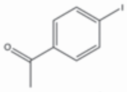
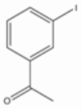
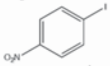
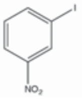
Entry	Iodoarene	Reaction time (h)	Isolated yield (%)
1		3	98
2		4	94
3		44	70
4		2	91
5		1	90
6		1	93
7		9	92
8		3	92
9		1	98
10		2	95
11		1	95
12		1	93

Table IV

Performance comparisons of catalysts in the reaction of iodobenzene and phenylacatylene under copper- and ligand-free conditions

Entry[ref]	Catalyst	Reaction conditions	Time (h)	Yield (%)
1(Roy, Senapati and Phukan, 2015)	$Pd\text{-}CoFe_2O_4$ (5 mol% Pd)	Ethanol, K_2CO_3, 70°C	6	90
2 (Komura, Nakamura and Sugi, 2008)	Pd-2QC-MCM-41 (0.18 mol% Pd)	NMP, piperidine, 80°C	3	99
3 (Cwik, Hell and Figueras, 2006)	Pd-MgLa (1.5 mol% Pd)	DMF, Et_3N, 90°C	10	90
4 (Borah and Dutta, 2013)	Pd0/montmorill-onite (0.07 mol% Pd)	CH_3CN, Et_3N, 82°C	3	90
5 (this paper)	$Pd_{0.02}Ce_{0.98}O_{2-\delta}$ (0.05 mol% Pd)	H_2O/CH_3CN (1:3), Et_3N, 82°C	3	98

phenylacetylene and iodobenzene. The catalyst was filtered off from the reaction mixture after 5 minutes and the hot filtrate was then allowed to react further under similar conditions. The reaction was then monitored every 15 minutes for 2 hours. Assessment of the rate of iodobenzene conversion from the fresh reaction and the hot filtration test suggests that the activity in the fresh reaction can be attributed to the Pd species in the solution (Figure 7). The fresh catalyst and the hot filtrate have almost identical reaction profiles (Figure 7). An ICP analysis of the filtered solution confirmed the presence of about 0.5 ppm of Pd in the hot filtrate.

Since the active catalytic phase was evidently the leached Pd, we attempted to determine the active Pd species using the mercury-poisoning test. Hg(0) is known to form amalgams with a variety of metals in their zero oxidation state (Reay and Fairlamb, 2015). Hence, if Pd dissociates from the solid $Pd_{0.02}Ce_{0.98}O_{2-\delta}$, it would bind with Hg(0) thereby quenching its catalytic activity. However, Pd in a raised oxidation state is not expected to be quenched by Hg(0) (Reay and Fairlamb, 2015). Thus, the mercury-poisoning test was used to establish whether bare Pd(0) did participate in catalysing the Sonogashira coupling reactions.

To do the mercury poison test for the system described here, the $Pd_{0.02}Ce_{0.98}O_{2-\delta}$ catalyst was filtered-off from the reaction mixture after a reaction time of 5 minutes and 2.5 mmol Hg(0) was added to the hot reaction mixture. The reaction mixture was then allowed to react further under similar conditions, while the activity was monitored every 15 minutes. It was found that no further reaction occurred after 15 minutes. Thus, the analysis confirms the presence of Pd(0) in the solution, which in turn gives insight into the reaction mechanism. Hence, the $Pd_{0.02}Ce_{0.98}O_{2-\delta}$ -catalysed Sonogashira coupling reaction is essentially a quasi-heterogeneous catalytic process occurring over solvated Pd(0) clusters.

The recycled catalyst showed about 60% conversion of iodobenzene in 2 hours. Hence, the recyclability test suggests that some of the leached Pd can redeposit on the CeO_2 support at the end of the Sonogashira reaction and/or the $Pd_{0.02}Ce_{0.98}O_{2-\delta}$ serves as an active catalyst reservoir.

Proposed mechanism

The exact mechanism by which the quasi-heterogeneous $Pd_{0.02}Ce_{0.98}O_{2-\delta}$ -catalysed copper- and ligand-free Sonogashira coupling reaction occurs is still under investigation. However, the catalytic activity results, leaching and recyclability tests seem to indicate that the reaction follows a Pd(0)/Pd(2+) mechanism (Scheme 2 – Figure 8). We proposed that the first step in the reaction mechanism is 'pre-activation' which allows $Pd^{2+}{}_{0.02}Ce_{0.98}O_{2-\delta}$ to enter the catalytic cycle as Pd^0/CeO_2. The Pd(2+) ions in the fresh catalyst are reduced *in situ* by triethylamine and/or the solvent system (H_2O/acetonitrile) to Pd(0). (Tougerti, Negri and Jutand, 2007; Jutand, Négri and Principaud, 2005) Since Pd(0) is more electron rich than Pd(2+), it allows for oxidative addition of the iodoarene, which marks the beginning of the catalytic cycle. The alkyne coordinates and forms a pi complex with Pd and then the desired Sonogashira coupling product is generated through the reductive elimination step.

Conclusion

In conclusion, we have developed a general and simple process for Sonogashira coupling reactions using

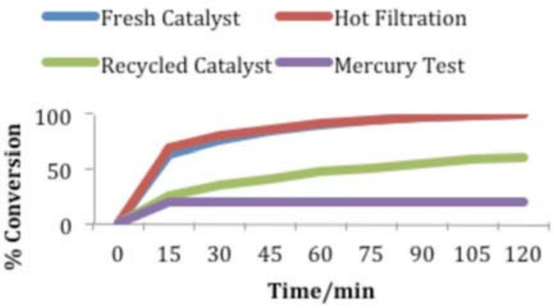


Figure 7—Reaction profiles of fresh catalyst, hot-filtration, recycled catalyst and mercury-poison tests

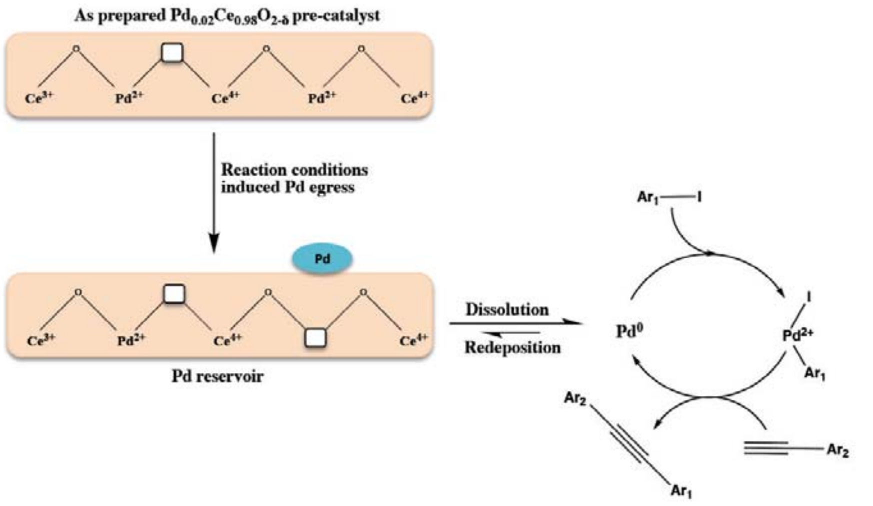


Figure 8—Scheme 2: A proposed reaction mechanism for $Pd^{2+}{}_{0.02}Ce_{0.98}O_{2-\delta}$ catalysed quasi-homogeneous Sonogashira cross-coupling reactions

$Pd_{0.02}Ce_{0.98}O_{2-\delta}$ as a precatalyst. The catalyst was found to be very effective in a water/acetonitrile solvent system at 82°C under ligand- and Cu-free reaction conditions. A wide range of iodorenes were coupled to phenylacetylene using this catalytic route. It was also found that the $Pd_{0.02}Ce_{0.98}O_{2-\delta}$ catalysed Sonogashira cross-coupling reactions are essentially a quasi-heterogeneous catalytic process occurring over solvated Pd(0) clusters. As a result, the recovered catalyst loses some activity upon recycle.

Experimental section

Cerium ammonium nitrate [$(NH_3)Ce(NO_3)_6$, 99.9%], palladium chloride [$PdCl_2$, 60%], urea [CH_4N_2O, 99.9%] were obtained from Sigma-Aldrich and were used without further purification.

Procedure for synthesis of $Pd_{0.02}Ce_{0.98}O_{2-\delta}$

The monophasic $Pd_{0.02}Ce_{0.98}O_{2-\delta}$ solid-solution oxide was prepared using a one-step urea-assisted solution combustion synthesis method described earlier (Cwele *et al.*, 2016). The catalyst synthesis method involved preparation of a redox combustion mixture composed of stoichiometric amounts of metal precursors [$(NH_4)_2Ce(NO_3)_6$ and $PdCl_2$] and urea [NH_2CONH_2] in the ratio of 1.0:3.77 respectively, dissolved in water. The solution was then stirred at 150°C for 10 minutes to evaporate water and reduce its volume to approximately
20 mL. The boiling solution was then introduced into a muffle furnace pre-heated at 400°C and was kept in the furnace overnight. A light brown solid was obtained.

Catalyst characterisation

A Bruker D8 Advance diffractometer, equipped with a XRK900 in-situ cell and a Cu K source (λ = 1.5406 Å) was used to record the powder X-ray diffraction patterns of the samples. The structures were refined by the Rietveld method using the Full Prof Suite-2000 program. The average crystallite size (D) and lattice strain (ε) of CeO_2 and $Pd_{0.02}Ce_{0.98}O_{2-\delta}$ were estimated from the modified Rietveld method and Williamson-Hall (W-H) plots.

ICP-OES was performed using a Perkin Elmer optical emission spectrometer Optima 5300 DV. Standards (1000 ppm Ce and Pd) were purchased from Fluka.

Brunauer–Emmett–Teller (BET) surface area measurements were determined using a MicroMetrics TriStar 3000 porosimeter with N2 as probe gas. About 0.4 g of each powder sample was degassed overnight at 200°C using a Micromeritics FlowPep 060 instrument prior to analysis.

SEM images were obtained with a Jeol JSM-6100 scanning electron microscope using a Bruker signal processing unit detector. The analysis was performed at random points along the surface of the catalyst. The samples were first mounted on aluminium stubs using double-sided carbon tape; they were then coated with gold using a Polaron E5100 coating unit.

For TEM analysis, the samples were viewed on a Joel JEM-1010 electron microscope. For high-resolution TEM (HR-TEM) and scanning electron microscopy (STEM) analysis, the samples were viewed on a Joel JEM-2100 electron microscope and the images captured were analysed using iTEM software. The powder samples were ultrasonically dispersed in ethanol and supported on a perforated carbon film mounted on a copper grid prior to analysis.

Catalyst testing: General procedure for sonogashira coupling reactions

A dry two-necked pear-shaped flask containing a stirrer bar, a condenser, 2 mL of H_2O and 6 mL of acetonitrile was charged with aryl halide (2.3 mmol), phenylacetylene (2 eq.), triethylamine (5 eq.) and catalyst $Pd_{0.02}Ce_{0.98}O_{2-\delta}$ (0.05 mol% Pd). The reaction mixture was stirred and (usually) heated to 82°C and its progress was monitored by GC and GC-MS. The iodoarene conversion was used to estimate the catalytic activity, using biphenyl 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. The organic layer was then evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel using

EtOAc/hexane (8/2) as an eluent. The structure of the coupling product was confirmed by ^1H and ^{13}C NMR spectroscopy and the results were consistent with those reported in the literature for substituted biphenylacetylenes (Djakovitch and Rollet, 2004).

General procedure for catalyst recovery and recyclability

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

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