

## Ce<sub>0.98</sub>Pd<sub>0.02</sub>O<sub>2-δ</sub>: Recyclable, ligand free palladium(II) catalyst for Heck reaction

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MS received 28 July 2010; revised 10 December 2010; accepted 16 December 2010

**Abstract.** Palladium substituted in cerium dioxide in the form of a solid solution, Ce<sub>0.98</sub>Pd<sub>0.02</sub>O<sub>1.98</sub> is a new heterogeneous catalyst which exhibits high activity and 100% trans-selectivity for the Heck reactions of aryl bromides including heteroaryls with olefins. The catalytic reactions work without any ligand. Nanocrystalline Ce<sub>0.98</sub>Pd<sub>0.02</sub>O<sub>1.98</sub> is prepared by solution combustion method and Pd is in +2 state. The catalyst can be separated, recovered and reused without significant loss in activity.

**Keywords.** Ionic Pd; carbon–carbon coupling; Heck reaction; Pd–ceria; heterogeneous catalysis.

### 1. Introduction

Palladium catalysed Heck reaction is well-known in organic synthesis.<sup>1</sup> Recent review article<sup>2</sup> has summarized the developments in homogeneous catalysed Heck reaction. Heck reaction is known for its high tolerance of functional groups and general applicability.<sup>3</sup> The palladium catalysed coupling reaction of organic halides with olefins allows a one-step synthesis of aromatic olefins<sup>4</sup>, which are used extensively as biologically active compounds, natural products, pharmaceuticals and precursors of conjugated polymers.<sup>5</sup> The Heck reaction proceeds in the presence of homogeneous as well as heterogeneous palladium catalysts, generated from either palladium(0) compounds or palladium(II) acetate or chloride salts.<sup>6</sup> Several ligands such as phosphines, phosphites, carbenes, thioethers have been successfully employed for this reaction.<sup>7</sup> However, homogeneous catalysis results in problems of recovery and reuse of the catalyst and also might result in palladium contamination of the product. Use of phosphines which are generally used as electron donating ligands in the Heck reactions is undesirable because they are toxic as well as moisture sensitive. Therefore, there is a need to develop catalysts which do not need any ligand for Heck coupling.

In recent years, Heck reaction has been catalysed by palladium metal supported on charcoal<sup>8</sup>, mesoporous carbon<sup>9</sup>, magnesium oxide<sup>10</sup>, silica, alumina or titania<sup>11</sup>, palladium/Nb-MCM-41<sup>12</sup>, polymers<sup>13</sup>, zeolites<sup>14</sup>, polyionic resins.<sup>15</sup> Basic supports such as layered double hydroxide<sup>16</sup>, basic zeolites<sup>17</sup>, alkaline exchanged sepiolites<sup>18</sup>, mixed oxide<sup>19</sup>, fluorapatite<sup>20</sup> have been used because Pd on these supports shows considerably higher activity towards Heck reaction compared to neutral supports. Noble metal ion substitution in reducible oxides such as CeO<sub>2</sub>, TiO<sub>2</sub> showed extraordinarily high activity for a variety of catalytic reactions.<sup>21</sup> We considered it worthwhile to see if Pd ion substituted CeO<sub>2</sub> can be used for carbon–carbon coupling reactions of aryl halides and substituted alkenes in N,N-Dimethylformamide (DMF) using K<sub>2</sub>CO<sub>3</sub> as a base and without any ligands. We show here that Pd<sup>2+</sup> ion in CeO<sub>2</sub> is an excellent Heck coupling heterogeneous catalyst without requiring any ligand. A wide range of substrates has been screened including the less active bromoaryl compounds. The product is 100% trans selective.

### 2. Experimental

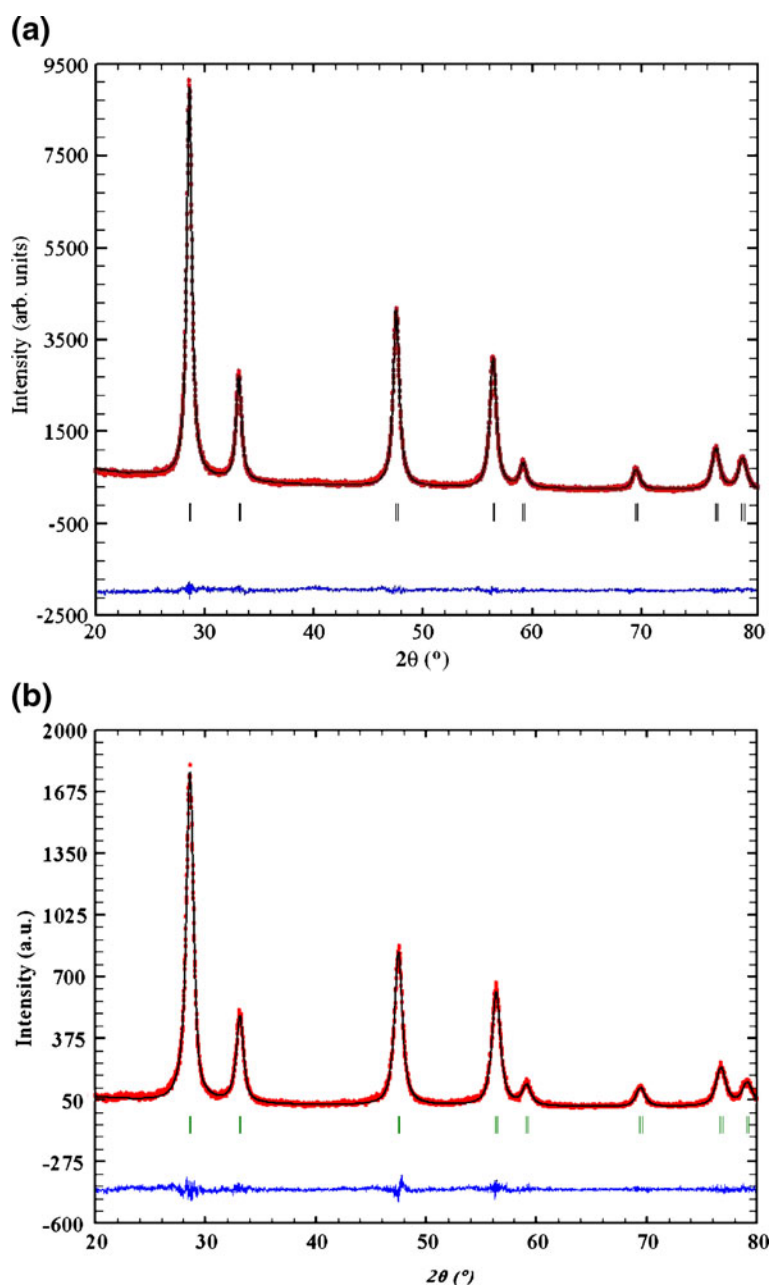
Ce<sub>0.98</sub>Pd<sub>0.02</sub>O<sub>1.98</sub> is prepared by solution combustion method as described earlier.<sup>22</sup> In a typical preparation

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9.8 mmol of  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$  (Loba Chemie Pvt. Ltd., Mumbai, India), 0.20 mmol of  $\text{PdCl}_2$  (Sigma Aldrich), 23.56 mmol  $\text{C}_2\text{H}_6\text{N}_4\text{O}_2$  (oxalyldihydrazide) were dissolved in 10 ml of water in a borosilicate dish with  $200\text{ cm}^3$  capacity. The dish containing the redox mixture was introduced into a muffle furnace maintained at  $350^\circ\text{C}$ . The solution boiled with frothing and foaming and ignited to burn with a flame ( $\sim 1000^\circ\text{C}$ ) yielding a voluminous solid product within 5 min. Catalysts before and after reactions were characterized by powder XRD (Phillips X'Pert diffractometer using

$\text{Cu K}\alpha$  radiation at a scan rate of  $2\theta=2^\circ/\text{min}$ ) and XPS (Thermoscientific Fisher Multilab 2000 using  $\text{Al K}\alpha$  radiation ( $1486.6\text{ eV}$ )).

All the aryl halides and olefins were obtained from S.D. Fine Chemicals Ltd. and Spectrochem Pvt. Ltd. Mumbai, India.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded using Bruker AV-400 MHz spectrometer. Chemical shifts were given in parts per million and coupling constants (J) in Hertz. Chemical shifts of  $^1\text{H}$  NMR are given with respect to the TMS chemical shift and of  $^{13}\text{C}$  NMR are given with respect to  $\text{CDCl}_3$



**Figure 1.** The Rietveld refined XRD patterns of  $\text{Ce}_{0.98}\text{Pd}_{0.02}\text{O}_{1.98}$ ; (a) before reaction, (b) after reaction.

chemical shift. Flash column chromatography was performed on silica gel (100–200 mesh) using ethyl acetate and hexane as eluents. The products were analysed employing gas chromatograph (Varian CP 3800 instrument). The capillary column used was Varian CP-Sil 8CB Fused silica column 5% Phenyl, 95% dimethylpolysiloxane Size: 30 m×0.25 mm (ID), 0.25 μm (Df).

### 2.1 Typical procedure for the Heck reaction

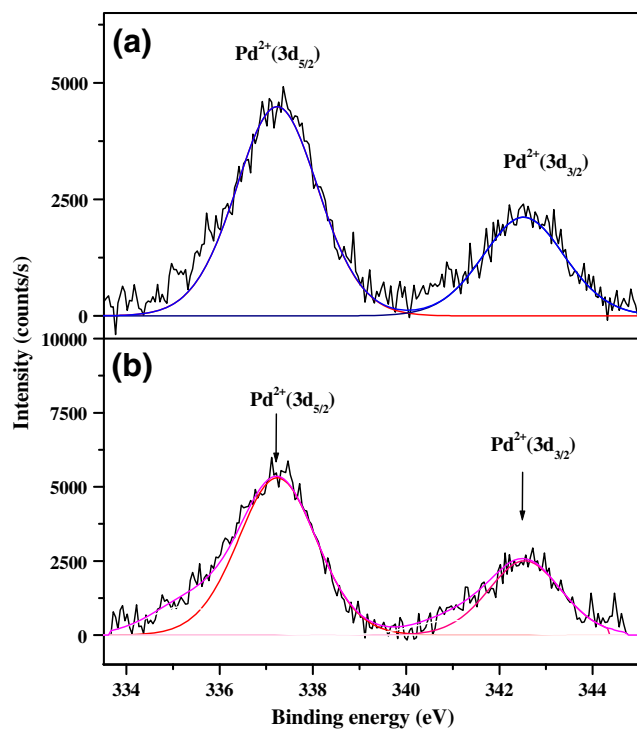
Under an atmosphere of nitrogen, an oven-dried two-necked 25 ml round-bottom flask containing a stir bar was charged with an aryl halide (0.50 mmol), olefin (2.25 mmol), catalyst Ce<sub>0.98</sub>Pd<sub>0.02</sub>O<sub>1.98</sub> (0.38 mmol, containing 7.6 μmol of Pd<sup>+2</sup> ions) and oven dried K<sub>2</sub>CO<sub>3</sub> (1.0 mmol). The mixture was heated and stirred at 120–130°C. The progress of the reactions was monitored by TLC. After completion of the reaction, the reaction mixture was cooled to room temperature and filtered. The filtrate is extracted with hexane and ethyl acetate (3:1) and water. The organic layer was washed with water and brine, dried with sodium sulphate and evaporated under reduced pressure. The residue was finally purified by flash chromatography

on silica gel. All the products have been fully characterized by NMR studies.

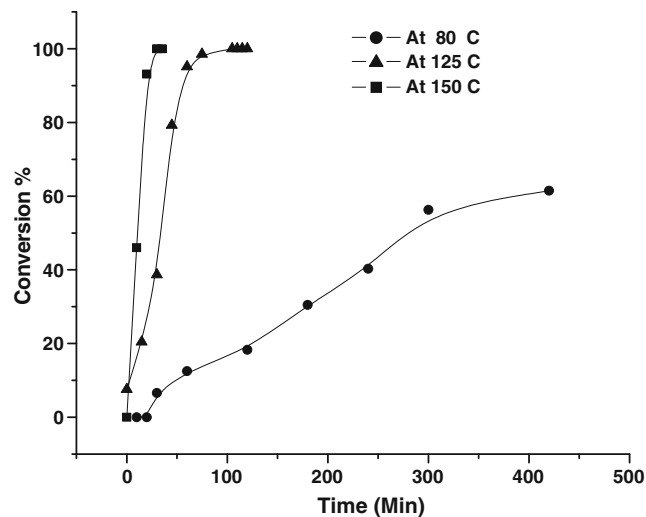
### 3. Results and discussions

Substitution of Pd<sup>+2</sup> ion in CeO<sub>2</sub> in the form of Ce<sub>0.98</sub>Pd<sub>0.02</sub>O<sub>2-δ</sub> solid solution has been shown earlier by XRD, XPS, EXAFS studies.<sup>22,23</sup> Rietveld refined XRD profile of freshly prepared compound is shown in figure 1(a). X-ray pattern corresponds to single phase Ce<sub>0.98</sub>Pd<sub>0.02</sub>O<sub>1.98</sub> as reported earlier.<sup>23</sup> From the FWHM of diffraction lines, crystallite size is estimated employing Schirrer formula ( $d=0.95\lambda/\beta\cos\theta$ ). Average size is 10±0.5 nm and colour of the catalyst is pale yellow. XPS of the Pd(3d) is shown in figure 2(a). Binding energy of Pd(3d<sub>5/2</sub>) at 337 eV confirms Pd in +2 state.<sup>22,23</sup> Cerium is in +4 oxidation state in this compound and is confirmed from the XPS of Ce(3d) (not shown). Thus the formula of the catalyst is Ce<sub>0.98</sub>Pd<sub>0.02</sub>O<sub>1.98</sub>. Due to lower valent Pd<sup>+2</sup> ion substitution for Ce<sup>+4</sup> ion in CeO<sub>2</sub>, oxide ion vacancies<sub>2</sub> are created. EXAFS study has confirmed that the oxide ion vacancy is found next to Pd<sup>+2</sup> ion in the lattice.<sup>23</sup>

The activity of nano-crystallite Ce<sub>0.98</sub>Pd<sub>0.02</sub>O<sub>1.98</sub> was examined for the Heck coupling reaction. Effect of reaction parameters such as time and temperature on the yield was investigated to determine the optimal condition with N,N-dimethylformamide (DMF), dimethylsulphoxide (DMSO), *N*-methylpyrrolidine (NMP) as solvents. The highest yield was obtained


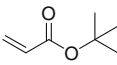
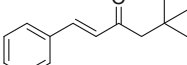


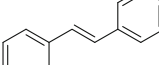


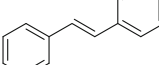

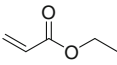
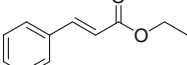


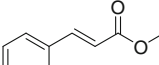
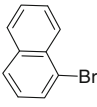
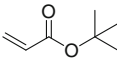
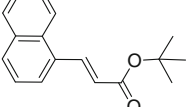
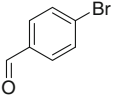
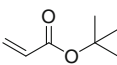
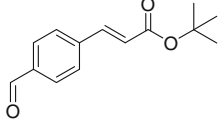
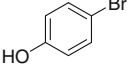
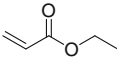
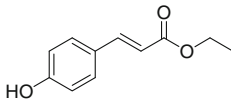
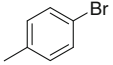
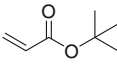
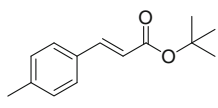
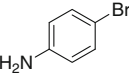
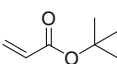
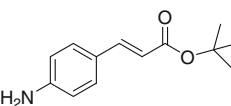
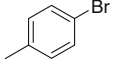

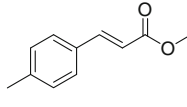
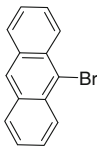

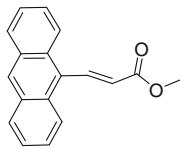

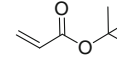
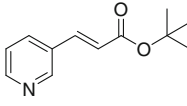


**Figure 2.** XPS of Pd(3d) core level region of Ce<sub>0.98</sub>Pd<sub>0.02</sub>O<sub>1.98</sub>; (a) before reaction, (b) after reaction.


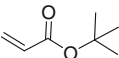
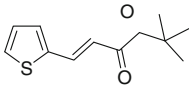

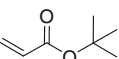
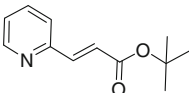

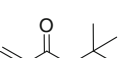
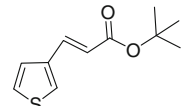


**Figure 3.** Conversion efficiency of reaction of iodobenzene and methyl acrylate at different temperatures. Yields are calculated based on GC results with respect to iodobenzene.

**Table 1.** Reactions of different aryl halides with different vinyl compounds.

Entry	Aryl halides	Olefins	Product	Temp(°C)	Time(h)	Yields <sup>a</sup>
1				120	5	82-49
2				130	6	63-85 <sup>b</sup>
3				140	7	51-59 <sup>b</sup>
4				120	5	83-01
5				120	5	86-98
6				140	10	93-45
7				130	6	95-22
8				140	10	52-02
9				140	10	46-21
10				140	10	65-23
11				140	10	48-56
12				140	10	86-54
13				130	6	92%

**Table 1.** (continued)

Entry	Aryl halides	Olefins	Product	Temp(°C)	Time(h)	Yields <sup>a</sup>
14				130	6	87%
15				140	10	76%
16				140	12	68%

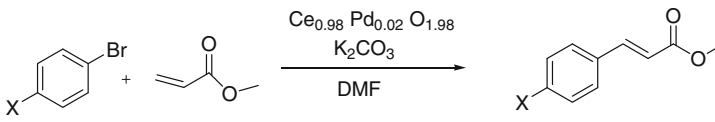
<sup>a</sup>The reaction was carried out with 0.50 mmol of aryl halide, 0.38 mmol of catalyst (7.6 μmol of Pd), 2.50 mmol olefins and 2 equiv. of K<sub>2</sub>CO<sub>3</sub> in DMF at 130°C.

<sup>b</sup>Isolated yields of pure product based on aryl halides.

in DMF and it was used as a solvent for all the reactions. All the reactions were carried out using potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) as a base except the reactions with styrene, for which sodium acetate was used. Iodobenzene and methylacrylate were chosen as model compounds for the initial study. A number of reactions have been carried out with Ce<sub>0.98</sub>Pd<sub>0.02</sub>O<sub>1.98</sub> catalyst and the reactions were performed with 5% molar excess of methyl acrylate at different temperatures. The aryl halides, olefins, products, time, temperature and yields are summarized in table 1. Heck reaction of iodobenzene with methyl acrylate

over pure CeO<sub>2</sub> as catalyst was carried out and there was no conversion. Thus, Pd ion in the catalyst is the active site for the Heck reaction in this catalyst. The C–X bond strength affects the activity towards the Heck reaction as the general cross coupling reactions follow C–I > C–Br > C–Cl. Yields of coupling reactions with alkyl acrylates were found to be more compared to styrene. Bromobenzenes with electron withdrawing groups have shown comparable activity with that of iodobenzene towards Heck reaction. Bromobenzenes substituted with electron donating group have shown lesser activity. Exclusively trans-coupled

**Table 2.** Reaction of acrylates with substituted bromobenzenes.

			
Entry <sup>a</sup>	X	Time (h)	Product (Yield %) <sup>b</sup>
1	H	6	72
2	CHO	6	95
3	COCH <sub>3</sub>	6	92
4	NH <sub>2</sub>	6	65
5	OH	6	62

R–methyl, ethyl, t-butyl

<sup>a</sup>The reaction was carried out with 0.50 mmol of aryl halide, 0.38 mmol of catalyst (7.6 μmol of Pd), 2.50 mmol olefins and 2 equiv. of K<sub>2</sub>CO<sub>3</sub> in DMF at 130°C.

<sup>b</sup>Isolated yields of pure product based on aryl halides.

product is obtained in each of the reaction as confirmed from NMR studies (see Supporting Information). The reaction of para-substituted bromobenzenes was studied with acrylates (table 2). 4-Formylbromobenzene and 4-acetyl bromobenzene underwent the reaction in 6 h with 95% and 93% yields respectively. But 4-bromoaniline and 4-bromophenols were relatively less reactive and the Heck product yields were 65% and 62%, respectively. However, unsubstituted bromobenzene gave more than 72% yield. The effect of temperature on conversion was studied with the iodobenzene and methyl acrylate as shown in figure 3. While ~100% conversion was obtained in 30 min at 150°C, it required nearly one hour when temperature was 125°C. However, at 80°C, the reaction was very slow that the conversion was ~60% even after 7 h.

It is important to compare the activity of this catalyst with those Pd substituted ligandless heterogeneous catalysts for Heck coupling in the literature. Turnover frequency is one simple way to compare the activity of the catalysts. Turnover frequency (TOF) is defined here as the ratio of moles of conversion per unit time per mole of palladium ion in the catalyst. TOF values were obtained for the reports in the literature for the reaction of iodobenzene and methyl acrylate and the values are compared with our catalyst in table 3. Clearly TOF of the present catalyst is higher compared to other Pd substituted ligandless heterogeneous catalysts for carbon-carbon cross coupling reactions reported in the literature.<sup>24</sup> TOF is comparable with recently reported immobilized Pd(OAc)<sub>2</sub> catalyst in ionic liquid on silica.<sup>25</sup> TOF of our catalyst reported here is for the first cycle. The same catalyst is reused and accordingly TOF will be much higher if we take

**Table 3.** Performance of the catalyst in the reaction of iodobenzene and methyl acrylate.

Entry	Catalyst (equivalents)	Time (h)	Yield (%)	TOF (h <sup>-1</sup> )
1 <sup>a</sup>	0.0103	5.5	91	16
2 <sup>b</sup>	0.0053	6.0	96	30
3 <sup>c</sup>	0.0024	8.0	91	48
4 <sup>d</sup>	0.0013	8.5	94	85
5 <sup>c</sup>	0.015	0.5	99	132

<sup>a, b, c, d</sup> Reported reactions Pd substituted ligandless heterogeneous catalysts found in literature (reference<sup>24</sup>).

<sup>e</sup> Our results: the reaction was carried out with 0.50 mmol of iodobenzene, 0.38 mmol of catalyst (7.6 μmol of Pd), 2.25 mmol methyl acrylate and 2 equiv. of K<sub>2</sub>CO<sub>3</sub> in DMF at 150°C.

**Table 4.** Reuse of catalyst.

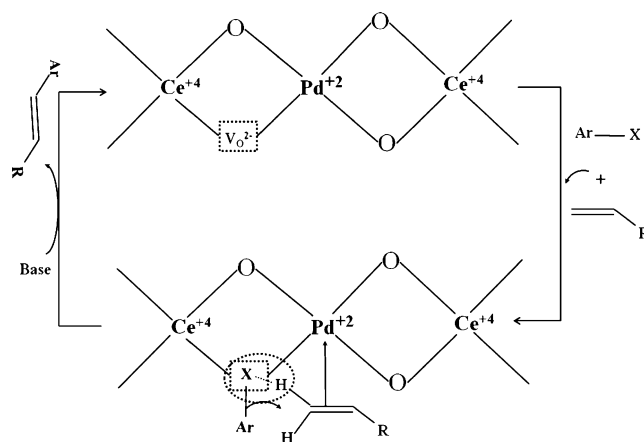
Run <sup>a</sup>	Recoverability	Product <sup>b</sup>
1	85 %	87 %
2	82 %	86 %
3	78 %	84 %

<sup>a</sup> The reaction was carried out with 0.50 mmol of iodobenzene, 0.38 mmol of catalyst (7.6 μmol of Pd), 2.25 mmol methyl acrylate and 2 equiv. of K<sub>2</sub>CO<sub>3</sub> in DMF at 130°C.

<sup>b</sup> Isolated yields of pure product based on iodobenzene.

into account the number of times the same catalyst is reused for the reaction.

The catalyst can be recycled without significant loss of activity. After the completion of the reaction, the catalyst was recovered by filtration or by centrifugation. The powder catalyst was washed with hexane to remove organic impurities and then with water to remove DMF and K<sub>2</sub>CO<sub>3</sub>. The dried catalyst was reused in a fresh reaction. There was no significant loss in the catalytic activity for the model reaction of iodobenzene and methyl acrylate (see table 4). In the same way we could recover and reuse the catalyst in all the reactions which are listed in table 1. The catalyst was examined after several cycles of reaction. The Rietveld refined XRD profile of this reused catalyst is shown in figure 1(b). Clearly, fluorite structure of the catalyst remains intact. Thus the catalyst is stable in the reaction condition. Further, XPS of the spent catalyst



**Figure 4.** Mechanism for carbon-carbon cross coupling reactions with Ce<sub>0.98</sub>Pd<sub>0.02</sub>O<sub>1.98</sub> catalyst.

was recorded and Pd(3d) spectrum given in figure 2(b) shows that Pd remains in +2 oxidation state. Pd ion is not reduced to Pd<sup>0</sup> state and Ce also remains in +4 state. Further, surface concentration of Pd ion has not changed indicating that Pd is not leached out. Pd ion is not leached out from the catalyst even in acid (0.1 N HCl) solution.

Catalyst surface contains two distinct sites: (i) electron deficient Pd<sup>2+</sup> ion for adsorption of donor molecules and (ii) oxide ion vacant sites next to Pd<sup>2+</sup> for the adsorption of acceptor molecules. There was no Heck reaction on pure CeO<sub>2</sub> clearly suggests that Ce<sup>4+</sup> and O<sup>2-</sup> sites are not active for this catalytic reaction. There are no other sites for the adsorption of donor and acceptor molecules in the catalyst. We have extensively shown that in Ce<sub>1-x</sub>Pd<sub>x</sub>O<sub>2-x</sub> the Pd ion and the oxide ion vacancies next to each other act as red-ox sites and dual site mechanism has been established.<sup>23</sup> Further, redox catalytic reaction such as CO+O<sub>2</sub> over this catalyst is shown to follow modified Langmuir–Hinshelwood mechanism where, CO is exclusively adsorbed on Pd<sup>2+</sup> site and oxygen on oxide ion vacancy site.<sup>21</sup>

A mechanism proposed for this ionic catalyst is given in figure 4. It is well known that olefins bind with Pd<sup>2+</sup> ion.<sup>26</sup> Thus, normal site for adsorption of olefin is Pd<sup>2+</sup> ion in Ce<sub>0.98</sub>Pd<sub>0.02</sub>O<sub>1.98</sub>. Oxide ion vacancy is a nucleophilic site ideal for accommodation of –Br, –I of the aryl halide. Elimination of HBr facilitated by the base leads to C–C coupling. Further studies are essential to see why only trans coupling is observed over this catalyst.

#### 4. Conclusion

A recyclable Pd<sup>2+</sup> ion substituted CeO<sub>2</sub> (Ce<sub>0.98</sub>Pd<sub>0.02</sub>O<sub>1.98</sub>) catalyses the carbon–carbon cross coupling of substituted iodobenzene, substituted bromobenzenes and bromoheteroaryls with alkylacrylates and styrenes with good yields.

#### Supporting information

NMR data of line products are given in the supporting information (see [www.ias.ac.in/chemsci](http://www.ias.ac.in/chemsci)).

#### Acknowledgments

This work was supported by the Department of Science and Technology (DST) and Council of Scientific and Industrial Research (CSIR), New Delhi. The authors also

thank the NMR Research Centre (NRC), Indian Institute of Science, for providing NMR spectra.

#### References

1. de Meijere A and Meyer F E 1994 *Angew. Chem. Int. Ed.* **33** 2379
2. Beletskaya A P and Cheprakov V 2000 *Chem. Rev.* **100** 3009; Whitcombe N J and Hii K K M, Gibson S E 2001 *Tetrahedron* **57** 7449
3. Crisp GT 1998 *Chem. Soc. Rev.* **27** 427; Dieck H A and Heck R F 1974 *J. Am. Chem. Soc.* **96** 1133
4. de Vries Johannes G 2001 *Can. J. Chem.* **79** 1086
5. Burke T R, Liu D G and Gao Y J 2000 *J. Org. Chem.* **65** 6288; Haberli A and Leumann C J 2001 *Org. Lett.* **3** 489; de Meijere A and Meyer F E 1994 *Angew. Chem.* **106** 2473
6. Biffis A, Zecca M, Basato M 2001 *J. Mol. Catal. A* **173** 249
7. Hillier A C, Grasa G A, Viciu M S, Lee H M, Yang C and Nolan S P 2002 *J. Organomet. Chem.* **653** 69; Selvakumar K, Zapf A and Beller M 2002 *Org. Lett.* **4** 3031; Yao C, Li H, Wu H, Liu Y and Wu P 2009 *Catal. Commun.* **10** 1099
8. Hallberg A and Westfelt L 1984 *J. Chem. Soc. Perkin Trans.* **1** 933
9. Wan Y, Wang H, Zhao Q, Klingstedt M, Terasaki O and Zhao D 2009 *J. Am. Chem. Soc.* **131** 4541.
10. Kaneda K, Higuchi M and Imanaka T 1990 *J. Mol. Catal.* **63** L33
11. Wali A, Pillai S M, Kaushik V K and Satish S 1996 *Appl. Catal. A* **135** 83
12. Mehnert C P, Weaver D W and Ying J Y 1998 *J. Am. Chem. Soc.* **120** 12289
13. Ding J H and Gin D L 2000 *Chem. Mater.* **12** 22
14. Djakovitch L and Koehler K 2001 *J. Am. Chem. Soc.* **123** 5990
15. Dams M, Drijkoningen L, Pauwels B, van Tendeloo G, de Vos D E and Jacobs P A 2002 *J. Catal.* **209** 225; Basu B, Das S, Das P, Mandal B, Banerjee D and Almqvist F 2009 *Synthesis* **7** 1137
16. Choudary B M, Madhi S, Chowdari N S, Kantam M L and Sreedhar B 2002 *J. Am. Chem. Soc.* **124** 14127
17. Corma A, Garcia H, Leyva A and Primo A 2003 *Appl. Catal. A* **247** 41
18. Ranting T, Shiding M, Zhimin L, Yun X, Buxing H, Guimin A and Kunlun D 2009 *Green Chem.* **11** 96
19. Cwik A, Hell Z and Figureas F 2006 *Adv. Synth. Catal.* **348** 523
20. Kantam M L, Shiva Kumar K B, Srinivas P and Sreedhar B 2007 *Adv. Synth. Catal.* **349** 1141
21. Hegde M S, Madras G and Patil K C 2009 *Acc. Chem. Res.* **42** 704 and references therein

22. Bera P, Patil K C, Jayaram V, Subbanna G N and Hegde M S 2000 *J. Catal.* **196** 293
23. Priolkar K R, Bera P, Sarode P R, Hegde M S, Emura S, Kumashiro R and Lalla N P 2002 *Chem. Mater.* **14** 2120
24. Mori K, Yamaguchi K, Hara T, Muzugaki T, Ebitani K and Kaneda K 2002 *J. Am. Chem. Soc.* **124** 11572; Molnar A, Papp A, Miklos K and Forgo P 2003 *Chem. Commun.* **20** 2626; Daku K M L, Newton R F, Pearce S P, Vile J and Williams J M J 2003 *Tet. Let.* **44** 5095; Phan N T S, Brown D H, Adams H, Spey S E and Styring P 2004 *Dalton Trans.* **9** 1348
25. Hagiwara H, Sugawara Y, Isobe K, Hoshi T and Suzuki T 2004 *Org. Lett.* **6** 2325; Hagiwara H, Sugawara Y, Hoshi T and Suzuki T 2005 *Chem. Commun.* 2942
26. Link JT and Overman L E 1998 *Metal-catalyzed cross-coupling reactions*, (eds.: F. Diederich, P. J. Stang) Weinheim; Wiley-VCHVerlag p. 231